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OF THE

ROYAL SOCIETY OF LONDON.

SERIES A

CONTAINING PAPERS OF A MATHEMATICAL OR PHYSICAL CHARACTER.

FOR THE YEAR 1897.

VOL. 189.

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THE Committee appointed by the *Royal Society* to direct the publication of the *Philosophical Transactions* take this opportunity to acquaint the public that it fully appears, as well from the Council-books and Journals of the Society as from repeated declarations which have been made in several former *Transactions*, that the printing of them was always, from time to time, the single act of the respective Secretaries till the Forty-seventh Volume; the Society, as a Body, never interesting themselves any further in their publication than by occasionally recommending the revival of them to some of their Secretaries, when, from the particular circumstances of their affairs, the *Transactions* had happened for any length of time to be intermitted. And this seems principally to have been done with a view to satisfy the public that their usual meetings were then continued, for the improvement of knowledge and benefit of mankind: the great ends of their first institution by the Royal Charters, and which they have ever since steadily pursued.

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  - *p.* Sternwarte.

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  - *p.* Royal Society of Tasmania.

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- Annapolis.
  - AB. Naval Academy.
- Austin.
  - *p.* Texas Academy of Sciences.
- Baltimore.
  - AB. Johns Hopkins University.
- Berkeley.
  - *p.* University of California.

United States (continued).

- Boston.
  - AB. American Academy of Sciences.
  - B. Boston Society of Natural History.
  - A. Technological Institute.
- Brooklyn.
  - AB. Brooklyn Library.
- Cambridge.
  - AB. Harvard University.
  - B. Museum of Comparative Zoology.
- Chapel Hill (N.C.).
  - *p.* Elisha Mitchell Scientific Society.
- Charleston.
  - *p.* Elliott Society of Science and Art of South Carolina.
- Chicago.
  - AB. Academy of Sciences.
  - *p.* Field Columbian Museum.
  - *p.* Journal of Comparative Neurology.
- Davenport (Iowa).
  - *p.* Academy of Natural Sciences.
- Ithaca (N.Y.).
  - *p.* Physical Review (Cornell University).
- Madison.
  - *p.* Wisconsin Academy of Sciences.
- Mount Hamilton (California).
  - A. Lick Observatory.
- New Haven (Conn.).
  - AB. American Journal of Science.
  - AB. Connecticut Academy of Arts and Sciences.
- New York.
  - *p.* American Geographical Society.
  - *p.* American Museum of Natural History.
  - *p.* New York Academy of Sciences.
  - *p.* New York Medical Journal.
  - *p.* School of Mines, Columbia College.
- Philadelphia.
  - AB. Academy of Natural Sciences.
  - AB. American Philosophical Society.
  - *p.* Franklin Institute.
  - *p.* Wagner Free Institute of Science.
- Rochester (N.Y.).
  - *p.* Academy of Science.
- St. Louis.
  - *p.* Academy of Science.
- Salem (Mass.).
  - *p.* American Association for the Advancement of Science.
  - AB. Essex Institute.
- San Francisco.
  - AB. California Academy of Sciences.

United States (continued).
- Washington.
  - AB. Patent Office.
  - AB. Smithsonian Institution.
  - AB. United States Coast Survey.
  - B. United States Commission of Fish and Fisheries.
  - AB. United States Geological Survey.

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- Washington (continued).
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  - *p*. United States Department of Agriculture.
  - A. United States Department of Agriculture (Weather Bureau).
- West Point (N.Y.)
  - AB. United States Military Academy.

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PHILOSOPHICAL TRANSACTIONS.

I. *A Magnetic Detector of Electrical Waves and some of its Applications.*

By E. Rutherford, *M.A.*, 1851 *Exhibition Science Scholar, New Zealand University, Trinity College, Cambridge.*

Communicated by Professor J. J. Thomson, *F.R.S.*

Received June 11,—Read June 18, 1896.

Introduction.

The present paper deals with the subject of the magnetization of iron by high-frequency discharges, and the uses of magnetized steel needles for detecting and measuring currents of very great rapidity of alternation.

It will be shown that these magnetic detectors offer a very simple means of investigating many of the phenomena connected with high-frequency discharges, and may be used over a wide range of periods of alternation. Not only may these detectors be used in ordinary Leyden jar circuits, but they also offer a sensitive means of investigating waves along wires and free vibrating circuits of short wave-lengths.

They were also found to be a sensitive means of detecting electrical radiation from Hertzian vibrators at long distances from the vibrator.

In the course of the paper the following subjects are investigated :—

I. Magnetization of iron by high-frequency discharges and the investigation of the effect on short steel needles.

II. Magnetic detectors and their uses.
  a. Detection of electro-magnetic radiation in free space.
    Waves were detected over half-a-mile from the vibrator.
  b. Waves along wires.
  c. Damping of oscillations.
    Resistance of iron wires.
    Absorption of energy by conductors.
  d. Determination of the period of Leyden jar discharges and the constants of the discharge circuit.

The magnetization of steel needles when placed in a spiral through which a Leyden jar discharge was passed has long been known.

In 1842 Professor HENRY was led to suspect from the anomalous magnetization of steel needles that the Leyden jar discharge was oscillatory.

Professor HENRY, ABRIA, and several others, used steel needles in their attempts to determine the direction of induced currents in secondary and tertiary circuits, when the Leyden jar was discharged through the primary, but with conflicting results.

Lord RAYLEIGH ('Phil. Mag.,' vol. 39, 1870, p. 429) made use of steel needles in a magnetizing spiral in investigating the maximum current of a break for ordinary induction circuits.

The general subject of the magnetization of iron, for rapid oscillatory currents, has been worked at by many different experimenters; Lord RAYLEIGH, using oscillatory currents of a frequency up to 1050 a second, showed that iron wires showed considerable increase of resistance, and deduced the value of the permeability of the wire. TROWBRIDGE ('Phil. Mag.,' 1891) has shown that iron wires rapidly damp down the oscillations of the Leyden jar discharge, and from his results deduced a rough value for the permeability of the specimens tested.

V. BJERKNES ('Electrician,' November 18, 1892) found that the damping out of oscillations in a Hertzian resonator takes place much more rapidly in a resonator of iron than when it is made of non-magnetic material.

Magnetization of Iron by a Leyden Jar discharge.

If a piece of steel wire, several centimetres in length, be taken and placed in a solenoid of a few turns, on the passage of a discharge the wire will be found to be magnetized. The magnetization is, in general, small, and increases slightly in amount when a succession of discharges are passed in the same direction.

Fig 1.

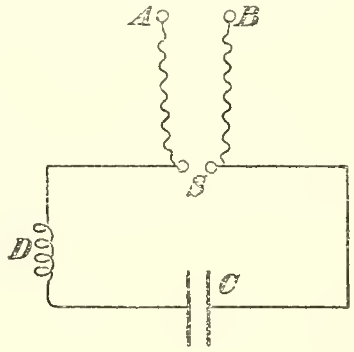


Fig. 1 shows the arrangement. A and B are the poles of a Wimshurst machine or an induction coil, C the condenser, S the air-break, and D the solenoid in which the steel wire is placed. The charging-up of the condenser before the spark passes was found to have no effect in magnetizing the needle.

In all experiments to follow, the magnetization of the needles was tested by means of a small mirror magnetometer. The needle was either fixed in position in the solenoid and the magnetometer placed beside it, or the needle removed and tested after each experiment. If wires of the same length but of different diameters be taken, it will be found that the magnetization is roughly proportional to the diameter of the wires. This is to be expected, since the magnetizing forces are confined to a thin skin on the surface of the needle, and so the amount of magnetization depends more on the surface than on the sectional area.

In order to determine accurately the way in which a piece of steel was magnetized from the surface inwards, recourse was had to a method of solution of the iron in acid. The needle to be tested was fixed in a glass vessel before a dead-beat magnetometer. Dilute hot nitric acid was poured in and kept at a constant temperature. As soon as the needle was covered it commenced to dissolve, and the variation of the deflection with the time was noted. In this way the amount and stages of the magnetization of the iron could be completely determined. From preliminary experiments on *uniformly* magnetized needles, it was found that under the action of the acid the diameter of the wire decreased uniformly with the time.

Let I represent the intensity of magnetization of a thin circular shell distant r from the centre of the needle, and M the deflection of the magnetometer at any instant.

$$\int_0^r \mathrm{I} \, . \, 2\pi r \, dr \text{ is proportional to M,}$$

therefore

$$\mathrm{I}r \text{ is proportional to } d\mathrm{M}/dr.$$

Let r be the radius of the wire at first. It has been shown that $a - r$ is proportional to t, the time of action of the acid.

Therefore

$$a - r = \kappa t \text{ where } \kappa \text{ is a constant,}$$

and

$$- dr = \kappa dt,$$

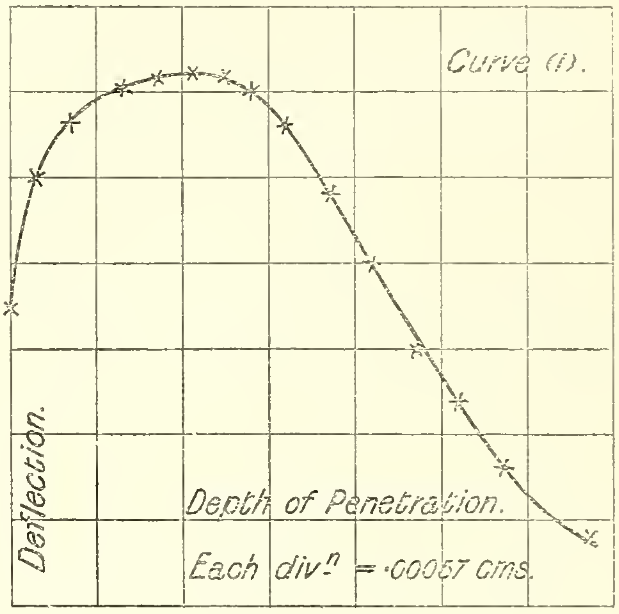
therefore

$$\mathrm{I} \text{ varies } \frac{1}{a - \kappa t} \, . \, \frac{d\mathrm{M}}{dt}.$$

If a curve be plotted whose ordinates represent the deflection and the abscissæ the time of action of the acid, $d\mathrm{M}/dt$ at any point is equal to the tangent of the angle which the tangent to the curve at that point makes with the axis of x. The variation of I can thus be completely determined from the experimental curve.

The following curve (Curve I) is an example of the magnetization of a piece of pianoforte wire, 4 centims. long, ·08 centim. in diameter, placed in a solenoid of two turns per centim. The frequency of the discharge was about 3 million per second.

The ordinates of the curve represent the deflection of the magnetometer and the abscissæ the depth to which the iron has been dissolved by the acid, measuring from the surface inwards. Each division of the ordinates corresponds to a depth = ·00057 centim.



The deflection of the magnetometer at first was 85 divisions. As the needle commenced to dissolve, the deflection increased rapidly to 156, remained nearly steady for a short time, and then rapidly diminished to zero; when this was the case the diameter of the needle was ·032 centim., so that the magnetization had penetrated to a distance of ·024 centim.

If the variation of the value of I, the intensity of magnetization from the surface inwards, be deduced from this curve, it will be seen that the surface layer is magnetized in one direction and an interior layer in the opposite direction. This apparently gives evidence of only two half oscillations, in opposite directions, in the discharge. A large number of needles were dissolved after magnetization under various conditions, and the same peculiarity was observed, although, from other evidence, it was known that there were a large number of vigorous oscillations before the discharge was much damped down.

When a needle magnetized to saturation was subjected to the discharge, the magnetization of the needle was always diminished, and on solution of the iron the same effect was observed, viz., a surface layer magnetized in the opposite direction to the internal magnetism.

Since a Leyden jar discharge in general gives several complete oscillations before it is greatly damped down, it would be expected that the surface layer of a uniformly magnetized needle would either be completely demagnetized or show evidence of several oscillations in opposite directions. The effect observed may be explained when the demagnetizing force of the ends of a short needle on itself is taken into account. The first half oscillation that tends to demagnetize the needle has the demagnetizing force of the needle assisting it, while the return oscillation has it in opposition. The return oscillation will therefore not be able to completely remagnetize the surface layer already affected, but a thin layer will be left in the interior. After the passage of the next oscillation another layer will be added in the same direction, and so on, till the final effect will be that the surface of the needle will be magnetized in the opposite direction to the interior.

If strongly-magnetized needles of the same diameter, but of different lengths, are taken and placed in the same solenoid, it will be found that the reduction of magnetic moment of the needle, due to the discharge, is greater the shorter the needle. This effect is due to the demagnetizing influence of the ends, which is greater the shorter the needle.

It was also found that if successive discharges be passed, the reduction of deflection gradually increases, till it reaches a steady state, so that the passage of any further number of discharges has no apparent effect on the magnetism of the needle.

The following table shows the effect of varying the length of the needle, the diameter being kept constant, and also the effect of successive discharges in each case.

Needle ·08 centim. in diameter; frequency about 3 millions.

Number of discharges.	10·5 centims.	6·4 centims.	3·2 centims.	1·6 centims.	·75 centim.
0	250	250	250	250	250
1	204	190	166	150	114
2	199	182	155	135	88
5	195	175	138	115	64
10	190	170	130	107	57
20	189	166	125	102	54
50	188	162	120	98	50

In the above table each of the needles was placed at such a distance from the magnetometer to give the same steady deflection of 250. The vertical columns show how the deflection fell after the passage of the different numbers of discharges. The vertical columns correspond to needles 10·5, 6·4, 3·2, 1·6, ·75 centim. respectively. For the needle 10·5 centims. long, the deflection fell from 250 to 188, while for the short needle, ·75 centim. long, the deflection fell from 250 to 50, although all the other conditions were precisely the same for each.

It will be observed from the above that the first discharge is mainly instrumental in reducing the deflection, and that after ten discharges have been passed, the deflection has nearly reached its final value.

Whenever a *magnetized* needle is placed in a solenoid and a discharge passed, there is always a reduction of the magnetization, the amount depending, for any given size of needle, on the intensity of the magnetic force in the solenoid and on the period of the oscillation. This is the case whether we are dealing with Leyden jar circuits, or the free vibrations, such as are set up in Hertzian receivers.

An unmagnetized needle, on the other hand, is not appreciably magnetized when placed in a circuit where the damping is small, for each successive oscillation destroys the effect of the previous one. Soft iron wires exhibit a similar effect to steel, only it is difficult to use wires of sufficient length to retain their magnetization. The effect on the needle is in general a purely surface one, and the amount of demagnetization does not bear any simple relation to the magnetizing force acting on it.

After every experiment, the needle was removed and placed in a solenoid and a steady current passed, sufficient to saturate the steel. In this way the needle could always be quickly reduced to the same state after any experiment, and it was found that, using hard steel wires, the results of successive experiments were very consistent with one another.

Passage of a Discharge Longitudinally through a Magnetized Wire.

If a piece of pianoforte wire, several centimetres in length, be taken and placed in series with the discharge circuit, in the passage of a discharge, the magnetic moment of the needle is diminished, due to the "circular" magnetization of the wire. If the needle be dissolved in acid, it will be found that there is a thin skin, apparently magnetized in opposition to the original magnetization, due to the resultant action of the demagnetizing force of the needle and the magnetic force due to the current in the wire.

The magnetic force H acting at any given point in the wire is given by

$$H = \frac{2\gamma}{r},$$

where γ is the current through the conductor flowing internal to the circle described through the point, and concentric with the surface of the conductor. The value at the surface of the wire is given by

$$H = \frac{2\gamma}{a},$$

where a is the radius of the wire.

Assuming μ, the permeability of the iron wire, as constant, the maximum value of the current at any point of the conductor decreases in geometrical progression as the distance from the surface inwards increases in arithmetical progression. As will be shown later in the part on "Resistance of Iron Wires," the current falls off even more rapidly than the theoretical law, on account of the increase of the value of μ as the amplitude of the current diminishes in intensity from the surface inwards.

For thin wires the magnetic force at the surface of the wire is much greater than for thicker ones. We should, therefore, expect a thick magnetized wire conveying the current to be affected to less depth than a thin one, and this is found to be the case.

A thin steel wire, ·025 centim. in diameter, was completely demagnetized by a discharge. In this particular case the maximum value of the current through the wire was about 100 amperes, and the value of the magnetic force at the surface of the wire was, therefore, about 1600 C.G.S. units. A hard steel wire, ·08 centim. in diameter, was only partially demagnetized, the deflection being reduced from 250 to 116 scale divisions.

The following are examples of a few of the experiments on the demagnetization of iron wires when the frequency of the discharge was about 3 million and the value of the maximum current about 100 amperes :—

1. Thin soft iron } Thin steel } wire diameter, ·025 centim. : completely demagnetized.
2. Steel wire : diameter, ·08 centim. : fall of deflection from 250 to 116.
3. Steel wire : ,, ·16 centim. : ,, ,, 250 to 184.
4. Steel wire : ,, ·25 centim. : ,, ,, 250 to 216.
5. Long hollow soft iron cylinder, $\frac{1}{4}$ millim. thick and diameter 1·8 millims.: fall of deflection from 250 to 230.

The same condenser and discharging current were used for all the specimens tested, and it is of interest to observe the depth to which the magnetism of the iron was affected by the discharge, assuming that the final deflection is that due to the mass of iron not circularly magnetized.

Wire.	Diameter.	Depth of penetration of the discharge.
	centim.	centim.
Hard steel wire . . .	·08	·013
Soft steel wire	·16	·011
Soft steel	·25	·009
Soft iron cylinder . . .	1·8	·0011

Experiments of this kind show to what a small depth the current penetrates into the iron wire. Very large momentary currents are conveyed through a surface skin of the conductor, and the intensity of the current diminishes rapidly inwards.

A thin magnetized steel wire was placed in the circuit of a small Hertzian plate vibrator. The deflection due to the needle fell from 300 to 250 after a succession of discharges.

This shows that the iron was unaffected below a depth of about ·0011 centim.

For rough comparisons of the intensity of currents in multiple circuits, the use of the "longitudinal" detector is often preferable to placing the needle in a solenoid.

A thin magnetized steel wire, placed in series with the circuit, is a surprisingly sensitive detector of oscillatory currents of small intensity.

In practice copper wires were soldered on to the extremities of the steel needle, which is placed in position before a magnetometer. A magnetizing solenoid is wound over the needle, and after every experiment a steady current was sent through in order to re-saturate the needle.

Both the "longitudinal" and "solenoidal" detectors may be very readily used to compare the intensities of currents in multiple circuits when the period of oscillation is the same for each. The best form of the solenoidal detector is explained later, and it has the advantage of being able to distinguish between the intensity of the first and second half oscillations.

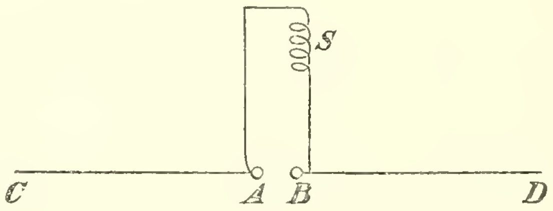
Detection of Waves in Free Space.

It has been shown that the amount of demagnetization of a magnetized needle depends on the fineness of the wire and the number of turns per centim. on the magnetizing solenoid.

If a short piece of thin magnetized steel wire be taken, and a large number of turns wound over it, it is a very sensitive means of detecting electrical oscillations in a conductor when the amplitude of the oscillations is extremely small. It was on this principle that a detector for electrical waves was devised, which proved to be a sensitive means of detecting Hertzian waves at considerable distances from the vibrator.

About twenty pieces of fine steel wire ·007 centim. in diameter, each about 1 centim. long, and insulated from each other by shellac varnish, formed the detector needle. A fine wire solenoid was wound directly over it, of two layers corresponding to about 80 turns per centim. As the solenoid was of very small diameter, about 15 centim. of wire served to wind the coil. This small detector was fixed at the end of a glass tube, which was itself fixed on to a wooden base, the terminals of the detector coil being brought out to mercury cups.

Fig. 2.



S (fig. 2) represents the detector needle and the solenoid wound over it. A and B are the mercury cups. CA and BD were two straight rods which served as receivers, one end of each being placed in the mercury cups.

The detector needle was strongly magnetized and placed before a small magnetometer, the deflection due to the needle being compensated by an auxiliary magnet.

If the receiving wires were parallel to the electric force of the wave from the vibrator, oscillations were set up in the receiver circuit, the surface layers of the needles were demagnetized, and there resulted a corresponding deflection of the magnetometer needle.

The amount of the deflection, of course, depended on the amplitude of the oscillations set up in the receiver, and, therefore, on the distance from the vibrator.

Long Distance Experiments.

When a Hertzian vibrator was used with plates 40 centims. square, and a short discharge circuit, quite a large deflection was obtained at a distance of 40 yards, the waves passing through several thick walls between the vibrator and receiver.

Further experiments were made to see how far from the vibrator electromagnetic radiation could be detected.

For the long distance experiments, the vibrator consisted of two zinc plates, 6 feet by 3 feet, and separated by a short discharge circuit of about 30 centims. When large plates were used, a Wimshurst machine was equally efficient as a Ruhmkorff coil for exciting the vibrations.

The first experiments were made over Jesus Common, Cambridge, the receiver being placed in one of the buildings on Park Parade. Quite a large effect was obtained at a distance of a quarter of a mile from the vibrator, and from the deflection obtained it was probable that an effect would have been got for several times that distance.

When the vibrator was set up in the top floor of the Cavendish Laboratory, a small, but quite marked effect was obtained at Park Parade, a distance of over half a mile in the direct line.

In this case the waves, before they reached the receiver, must have passed through several brick and stone walls, and many large blocks of buildings intervened between the vibrator and receiver. The length of wave given out by the vibrator was probably six or seven metres, and a wave of that length seemed to suffer very little loss of intensity in passing through ordinary brick walls.

From an experiment tried in the Cavendish Laboratory it was found that the effect of six solid walls and other obstacles between the vibrator and receiver did not diminish the effect appreciably. When the vibrator was working in the upper part of the Laboratory, a large effect could be obtained all over the building, notwithstanding the floors and walls intervening.

A large number of experiments were made on the effect of varying the length and diameter of the receiving wires. If a fairly dead-beat vibrator were used, *e.g.*, plates with a short inductance, it was found that the deflection gradually increased with increase of length of the receiving wires, reaching a maximum which was unchanged by any further increase of length.

The effect on the detector was found to be practically independent of the sectional area of the receiving wires. A thin wire and a thick rod of the same length had equal effects; a plate of metal, 6 centims. wide, produced the same deflection as a thin wire.

If two wires instead of one were used in parallel the effect was the same as one, though the wires were some distance apart. Any number of wires in parallel had the same effect as a single wire or plate.

No difference could be detected whether the first half oscillation in the receiver tended to magnetize the needle or the reverse. Since the vibrator used was nearly dead-beat, this shows that the damping of the oscillations in the receiver is very small. On introducing a short carbon rod in the circuit the deflection was greatly reduced.

It was found impossible to magnetize soft iron or steel when placed in the receiving circuit on account of the slow decay of the amplitude of the oscillations. The detector needle may be kept in position for a succession of observations, provided the current in the receiving circuit is steadily increasing for each experiment, otherwise the detector should be remagnetized and placed in position again after each observation. The deflection was found to be very constant for a series of experiments under the same conditions.

The connection between the intensity of the electric force at the receiver and the deflection of the magnetometer needle can be easily determined by swinging the receiving wires through different angles.

When the receiver is placed symmetrically with regard to the vibrator, the deflection was a maximum when the receiving wires were parallel to the axis of the vibrator, and the intensity of the electric force acting along the receiver varies as the cosine of the angle from the maximum position.

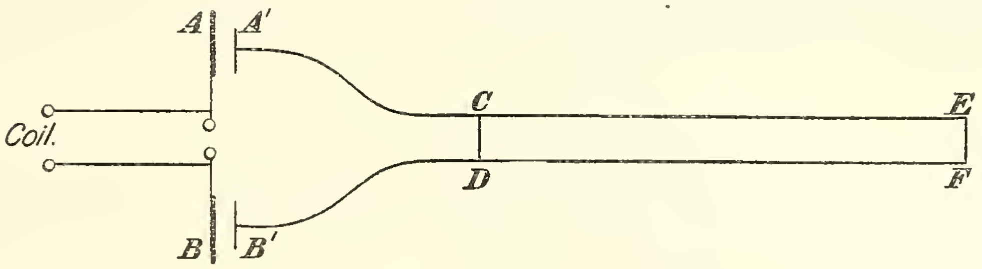
With plate vibrators the deflection was found to be nearly independent of the degree of brightness of the spark terminals and remained sensibly constant for long intervals. In the case of the small cylindrical vibrator used by HERTZ with the parabolic reflectors, the deflection continually varied with the state of the sparking terminals, and such small vibrators cannot be relied on for metrical experiments.

Some experiments were made to see if the magnetic force in the wave front could be directly detected. A collection of thin wires, insulated from each other and magnetized to saturation, were used and placed in the direction of the magnetic displacement, but the values of the magnetic force were too small to be observed, except quite close to the vibrator.

Waves along Wires.

It was found that the use of a detector, composed of fine insulated wires, was quite delicate enough to investigate waves along wires when there was only one turn of wire round the detector needle. Since the reduction of magnetic moment was nearly proportional to the amplitude of the current, the intensity of currents at various points could be very approximately compared.

Fig. 3.



The ordinary Hertz arrangement (fig. 3) was set up for obtaining free vibrating circuits.

A and B were two plates set up vertically. Beside them were two small plates A′ and B′, and long wires A′E, B′F were led from these plates. A fixed bridge was placed at EF, the ends of the wires, and a detector placed at the middle point of EF, with a small magnetometer fixed in position.

A sliding bridge, CD, was then moved till the fall of the deflection of the detector needle was a maximum. This position of the bridge could be very accurately determined, for a movement of the bridge through 1 centim. altered the deflection considerably. The detector was then placed in various parts of the circuit CE, and the amplitude of the current at the different points determined. It was found that the current was a maximum at C and the middle point of EF. A well-defined node was found at the middle point of CE.

The length CEFD was thus half a wave-length.

Since the use of the bolometer has been the only means of accurately investigating waves along wires, it was interesting to observe whether the magnetic detectors were of the same order of sensitiveness as the bolometer.

One turn of wire was wound round each of two glass tubes, sliding along the wires CE and DF, as in Reuben's experiments. Instead of the fine bolometer wire, a detector needle, with several turns of wire around it, was placed in series with the two turns of wire. The charging and discharging of the small condensers, formed by the straight wires and the small coils around them, was quite sufficient to almost completely demagnetize the needle. By this method the movement of extremely small quantities of electricity could be detected and the sensitiveness was quite comparable with that of a delicate bolometer.

No appreciable damping could be detected for the long wire circuits, showing that they were probably vibrating almost independently of the primary vibrator.

If a metre or two of wire was fixed to the pole of a Wimshurst machine, on the passage of a spark, there was evidence of a rapidly-oscillating current set up in the wire. By using a sensitive detector, with a few turns round it, the variation of the current along the wire could readily be determined.

If short lengths of wire were fixed to any portion of a Leyden jar circuit, on the passage of a discharge, there was always evidence of a rapid oscillation set up in the wire. Each of the short circuits had a tendency to vibrate in its own natural period, but the results were complicated by the oscillations of the main circuit.

Damping of Oscillations.

The use of magnetized needles offers a simple and ready means of determining the damping of oscillations in a discharge circuit.

Let L be self-inductance of discharge circuit for rapid currents.
,, C = capacity of condenser.
,, R = resistance of leads and airbreak to the discharge.
,, V_0 = potential to which condenser is charged.

The current γ at any instant is given by

$$\gamma = \frac{CV_0}{(LC)^{\frac{1}{2}}} e^{-R/2L \cdot t} \sin \frac{t}{(LC)} .$$

The exponential term only includes the case of frictional dissipation of energy, and does not take into account radiation into space. In the experiments at present considered, where the condenser is of the type of a Leyden jar, there can be but very small amount of dissipation of energy due to radiation.

Assuming R to be constant, the amplitude of the current decays in geometrical progression.

Consider two similar small oppositely wound solenoids A and B placed in series in the discharge circuit. Two magnetized needles are placed in A and B, the north poles facing in the same direction. After the passage of a discharge, it will be found that the reduction of magnetic moment is not the same in the two needles.

Let $\alpha_1 \alpha_2 \alpha_3$ . . . be the half-oscillations of the discharge in one direction.
,, $\beta_1 \beta_2 \beta_3$ . . . be the half-oscillations in the opposite direction.

Suppose that the half-oscillation α_1 tends to magnetize the needle in the solenoid A still further. Since the needle is saturated no effect is produced. β_1 demagnetizes the surface skin, α_2 tends to remove the effect of β_2, and so on. In the solenoid B α_1 demagnetizes the needle, β_1 tends to remagnetize it in its original direction, and so on. Since the maximum value of the current of α_1 is greater than the maximum value of β_1, the needle in B will be more demagnetized than in A.

If, however, we increase the number of turns per centimetre on the solenoid A, until the effects on the two needles are exactly the same, then *assuming* that the value of the current decreases in geometrical progression, the maximum value of the magnetic force due to the oscillation β_1 acting on the needle A is equal to the maximum value due to the oscillation α_1 on β.

Let $\gamma_1\gamma_2$ be the maximum values of the current in the first and second half-oscillations respectively.

Let n_1n_2 be the number of turns per centimetre on solenoids A and B respectively.

Then, since

$$4\pi n_1\gamma_1 = 4\pi n_2\gamma_2, \qquad \gamma_2/\gamma_1 = n_1/n_2.$$

the ratio of the second to the first half-oscillation is therefore known, and the damping is thus determined. The actual resistance in the circuit may also be deduced.

Now $\gamma_1 = pCV_0e^{-R/2L\,.\,T/4}$ where T = period of complete oscillation and $p = \frac{1}{(LC)^{\frac{1}{2}}}$,

$\gamma_2 = pCV_0e^{-R/2L\,.\,3T/4}$.

Therefore

$$e^{-R/2L\,.\,T/2} = \frac{\gamma_2}{\gamma_1} = \rho_1, \text{ say}.$$

Therefore

$$\log \rho_1 = -\frac{R}{2L}\cdot\frac{T}{2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1).$$

Since L and T are known from the constants of the discharge circuit, and ρ_1 is determined by experiment, R is known.

In practice, in order to avoid the necessity of determining the constants of the discharge circuit, an additional known resistance r is introduced into the circuit. If an electrolytic resistance of zinc sulphate with zinc electrodes be used, the resistance will be found to be practically the same for steady as rapidly alternating currents, as the specific resistance is very great.

Let ρ_2 be the ratio of the amplitudes of the two half oscillations when $R + r$ is in the circuit

$$\log \rho_2 = -\frac{R+r}{2L}\cdot\frac{T}{2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2).$$

Dividing (2) by (1)

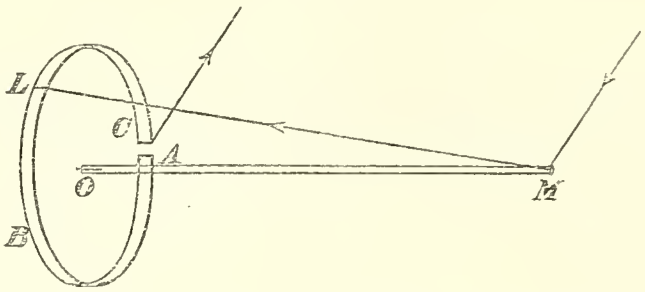
$$\frac{R+r}{R} = \frac{\log \rho_2}{\log \rho_1},$$

R is therefore determined in term of r, a known resistance.

The method of two solenoids was not adopted in practice, but one theoretically equivalent employed.

A narrow piece of sheet zinc ABC was taken (fig. 4) and bent into almost a complete circle of 7 centims. diameter. This was fixed on a block of ebonite. At the centre of the circle a thin glass tube OM was placed, which served as the axis of a metal arm LM, which pressed against the circumference of the circle and could be moved round it. The "detector" consisted of about thirty very fine steel wires, ·003 inch in diameter, arranged into a compound magnet about 1 centim. long. The wires were insulated from each other by shellac varnish, and the small needle was fixed inside a thin glass tube which could be easily slipped in and out of the central glass tube OM.

Fig. 4.



A divided scale was placed round the circumference ABC, and the whole arrangement was fixed in position before a small mirror magnetometer. The magnetized "detector" needle was placed in position by sliding it in the glass tube, and the deflection due to the needle was compensated by another magnet. The wires of the discharge circuit were connected to C and M, and when the arm ML was at C no effect was produced on the needle. When the discharge passed round the circle there was a deflection due to the partial demagnetization of the detector. The detector was then quickly removed and magnetized to saturation in an adjacent solenoid and then replaced. It was found that, provided the detector was magnetized in a very strong field, on replacing it in position the zero remained unchanged, and the same deflection was obtained time after time for similar discharges.

Since the magnetic field at the centre of a circle due to an arc of length l is given by

$$H = \frac{l\gamma}{r^2}, \text{ where } \gamma \text{ is the current,}$$

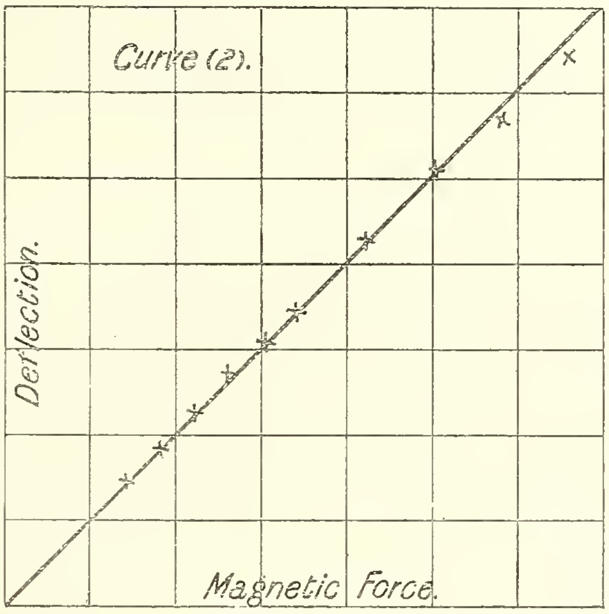
we see that the magnetic force acting on the needle is proportional to the length of the arc traversed by the discharge.

A series of observations were made and it was found that the deflection due to the detector was approximately proportional to the magnetic force acting on the needle, provided the magnetic force was well below the value required to completely demagnetize the steel.

Curve (2) represents the relation between the deflection of the magnetometer and the magnetic force acting on the needle. The curve is nearly a straight line except near the top part of the curve.

To determine the damping of the oscillations a discharge was passed in one direction and the deflection noted. The detector was removed, magnetized and replaced. The direction of the discharge was reversed and the arm of the circle moved until the deflection was the same as before. When this is the case the ratio of the maximum values of the first and second half oscillation is given by the ratios of the arcs traversed by the discharge.

In this way the rate of decay of oscillations in ordinary discharge circuits was examined. With short air breaks and copper wires for connection, it was found that the damping was hardly appreciable. As the length of the spark gap was increased, the absorption of energy in the air-break caused the oscillations to damp rapidly.

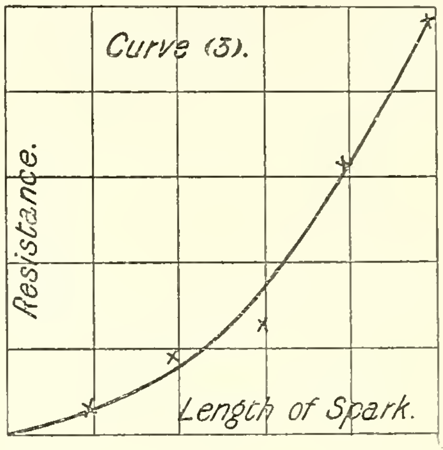


If the copper wires of the discharge circuit were replaced by iron wires, there was in all cases a very rapid decay of the oscillations, whatever the length of the air-break. If an iron cylinder were placed in a solenoid, the absorption of energy by the cylinder caused a rapid damping, while a copper cylinder of the same diameter had no appreciable effect.

Experiments on Damping of Oscillations. Discharge circuit rectangular, 184 centims. by 90 centims.; Self inductance of circuit, L = 7,400; Capacity, C = 2,000 electrostatic units; Frequency, 1·25 millions per second.

Length of spark gap.	Ratio of amplitudes of two first half oscillations.	Resistance.
centim.		ohms.
·06	·98	—
·12	·97	1·1
·24	·93	2·6
·37	·9	3·7
·49	·79	8·4
·61	·7	12·4

In the third column the apparent resistance, corresponding to the absorption of energy in the conducting wires and spark gap is tabulated. The calculated value of the resistance of the wires of the discharge circuit was ·4 ohm, so that the remainder of the resistance is due to the great absorption of energy in the air break.



The above curve represents the relation between the length of the spark and the apparent resistance that the spark offers to the discharge. The ohmic resistance of the air break is probably very variable, depending on the intensity of the charge at any instant, but the absorption of energy is quite definite and may be expressed in terms of the non-inductive resistance which, when placed in the circuit, would absorb the same amount of energy.

It will be observed that the damping of the oscillations increases rapidly with the length of the spark, and that the resistance of the air break increases very rapidly with its length.

It was also found that the damping depended on the capacity when the inductance and spark length were kept constant. The damping and also the resistance of the spark were found to increase with increase of capacity. For example with an air break of ·32 centim. the damping and resistance are given below.

Capacity.	Ratio of Oscillations.	Resistance.
1000	·94	2·2
2000	·9	2·6
4000	·81	3·8

When the capacity of the circuit was small the damping was found to be very small. If iron wires were put into the place of the copper wires in the discharge circuit, the damping was found to be great for all capacities investigated.

When the capacity of the circuit was only 130 electrostatic units, and inductance 2400, no appreciable damping was found for an air break ·5 centim.: When the copper wire was replaced by an iron one of the same dimensions, the second half-oscillation was only ·6 of the amplitude of the first.

Resistance of Iron Wires for High Frequency Discharges.

The rapid decay of the oscillations when iron wires formed the discharge circuit has been already noted. This has been observed by TROWBRIDGE ('Phil. Mag.,' December, 1891), who found, by photographing the spark, that there was evidence of much fewer oscillations when iron wires were used instead of copper.

For very rapid oscillations the resistance R′ is given by $R' = \sqrt{\frac{1}{2}p\mu l R}$ (see Lord RAYLEIGH, "On the Self-Induction and Resistance of Straight Conductors," 'Phil. Mag.,' 1886), where R is the resistance of the wire for steady currents, l the length of the wire, μ the permeability, and $p = 2\pi n$, where n is the number of oscillations per second.

Since the expression involves μ, we should expect the resistance to be much greater for iron wires than for wires of the same conductivity, but non-magnetic.

To determine the resistance of iron wires a very simple method was used. The fall of deflection, due to the detector needle, arranged as in (fig. 2) was noted. The iron wire was then removed and a copper one of the same diameter substituted. Since the inductance of the circuit was practically unchanged, if the damping in the two circuits are equal, the resistances should be the same. A short piece of high-resistance platinoid wire was introduced into the circuit of the copper wire, and the length adjusted until the deflection was the same as in the first case. When this is so, the resistance of the platinoid wire, together with the resistance of the copper wire, is equal to the resistance of the iron wires for the frequency employed.

The resistance of the copper wires was calculated for the frequency used, but was, in general, small compared with the resistance introduced.

The resistance of the platinoid wire was also calculated, but was found to be practically the same as for steady currents. The length of wire placed in the current was 265 centims. ; spark length was ·25 centim.

Kind of wire.	Diameter.	R.	R_1.	R_1/R.
	centims.			
Soft iron	·025	6·1	11·8	1·9
"	·047	2·62	12·8	4·9
"	·094	·57	9·2	16
"	·295	·051	4·2	72
Pianoforte steel wire . . .	·062	1·51	11·3	6·5
Nickel wire	·062	·66	3·7	5·9

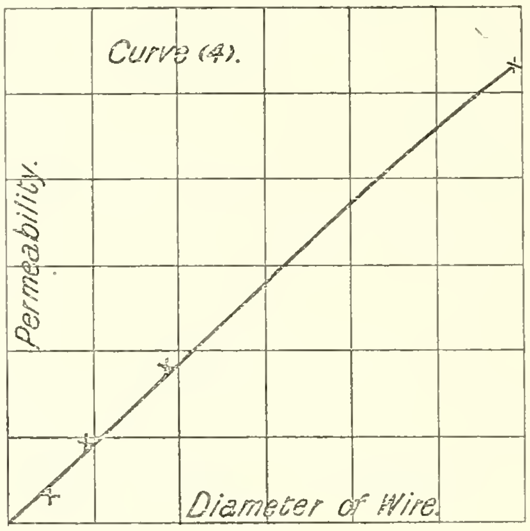
In the above Table, R is the resistance for steady currents, R_1 the resistance for a frequency 1·6 millims. per second. The last column gives the ratio R_1/R for the different wires. In the case of the wire ·295 centim. in diameter, the resistance is 72 times the resistance for steady currents, while in the case of the wire of ·025 centim. diameter, it is only 1·2 times.

If the value of μ, the permeability of the specimens of soft iron, be calculated from the formula

$$R' = \sqrt{\tfrac{1}{2}p\mu l R},$$

it will be found that the value varies with the diameter of the wire.

Diameter.	μ.
centims.	
·025	3·5
·042	9·4
·094	18
·295	53



The above curve (Curve 4) shows the relation between the diameter of the wire and the permeability for the discharge. It will be seen that μ varies approximately as the radius of the wire.

The very small value of the permeability for fine wires is to be expected when we consider the very large currents that pass through the wire, and the consequent large value of the magnetic force that acts at the surface of the iron.

The maximum current of discharge, assuming the damping to be small, is given by

$\gamma = pCV_0$, where C is capacity and V_0 the potential to which condenser is charged.

In the above experiments the air-break was about $\frac{1}{10}$ inch, and the difference of potential about 10,000 volts, and since $p = 5 \cdot 10^6$, $C = 4000$, the maximum current was about 222 amperes.

The magnetic force at the surface of the wire of radius r, which conveys the current, is given by

$$H = \frac{2\gamma}{r} = 3552 \text{ C.G.S. units, if } r = \cdot 0125 \text{ centim.}$$

If we assume the value of B to be about 14,000, we see that the permeability for the extreme surface layer would be about 4. The value of the magnetizing force diminishes from the surface inwards, so that the mean permeability of the iron to the discharge should be greater than the value at the surface. These considerations show that the permeability of iron to these discharges is by no means constant, but depends on the diameter of the wire and the intensity of the discharge.

The resistance of iron wires was found to vary with the length of the spark. Short air-breaks gave higher values of the resistance than long ones. When the length of the spark was so adjusted that the maximum current was approximately constant for different periods, the resistance was found to vary as the square root of the frequency, as we should expect from theory.

Several specimens of pianoforte steel wire were examined to see whether the larger waste of energy due to hysteresis in steel materially affected the value of the resistance, but the increase of resistance was not so great as for soft iron wires of the same diameter, although the loss due to hysteresis in steel is much greater than in soft iron for slow cycles.

Absorption of Energy by Metal Cylinders.

This subject has been treated mathematically and experimentally by J. J. THOMSON ('Recent Researches,' p. 321–326). It is there shown by observing the electrodeless discharge that a cylinder of iron placed in a solenoid absorbs considerably more energy than a copper one of the same dimensions. The method adopted here admitted of quantitative as well as qualitative results.

An ordinary Leyden jar was discharged through a solenoid of about thirty turns and 14 centims. long. The metal cylinder was then placed in the solenoid and the damping of the oscillations observed. The cylinder was then removed and a non-inductive resistance added until the damping was the same as when the metal cylinder was in the solenoid. The absorption of energy in the cylinder was then equal to the absorption of energy in the added resistance, whose value was known. In the above we have taken no account of the change of inductance of the circuit due to the metal cylinder being placed in the solenoid. The change is small, and could be made negligible by making the inductance of the solenoid small compared with the rest of the circuit.

(1.) A test-tube was filled with finely laminated iron wire, ·008 inch in diameter. The test-tube was filled with paraffin oil, to insure insulation from eddy currents.

The absorption of energy in this case corresponded to an added resistance of 10·25 ohms to the circuit.

(2.) A test-tube filled with steel filings and insulated as in (1). Increase of resistance, 9 ohms.

(3.) A thin soft iron cylinder, 1·9 centims. in diameter. Increase of resistance, 3·9 ohms.

(4.) Solid iron rod. Increase of resistance, 3·3 ohms.

(5.) A copper cylinder, a test-tube filled with a copper sulphate solution, and a platinum cylinder showed no appreciable absorption of energy.

(6.) A carbon rod absorbed a large amount of energy. Increase of resistance, 3·3 ohms.

TABLE of Absorption of Energy of various Conductors; Absorption of Energy expressed in Terms of the Increased Resistance of the Discharge Circuit.

Substance.	Increase of resistance.
Laminated soft iron wires . . .	10·25 ohms
Solid soft iron cylinder	3·5 ,,
Hollow iron cylinder	3·9 ,,
Carbon cylinder	3·3 ,,
Copper, platinum, zinc cylinders .	not appreciable
Steel filings	9 ohms

The frequency of the oscillations in the above experiment was two million per second.

If the experimental value obtained for the increase of resistance due to the solid iron cylinder be compared with the theoretical value ('Recent Researches,' p. 323), the value of the permeability will be found to be 172, which accounts for the much greater absorption by an iron cylinder than a copper one.

From the peculiar deadened sound of the spark, it could always be told when much energy was being absorbed in the discharge circuit. With copper wires for the discharge circuit, the spark was sharp and bright; when iron wires were substituted, the spark was weak; when an iron cylinder was put in the place of a copper one, the spark was neither so bright, nor so sharp in sound.

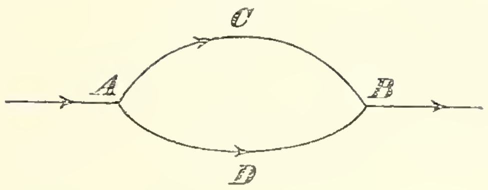
Determination of the Period of a Discharge Circuit.

It is often a difficult matter to obtain even an approximation of the period of oscillation of a discharge circuit when the capacity of the condenser and the self-inductance of the circuit cannot be directly calculated.

The following simple method was found to work very accurately in practice, and could be used for a fairly wide range of frequencies.

Let ACB, ADB (fig. 5) be two branches of a discharge circuit in parallel, R and L the resistance and inductance of the branch ACB, S and N the resistance and inductance of branch ADB.

Fig. 5.



Let M be the coefficient of mutual inductance between the two branches.

Let x and y be currents in branches ACB, ADB respectively.

It is shown ('Recent Researches,' p. 513) that for a rapidly-alternating current of frequency n, where $p = 2\pi n$, that

$$x = \left\{\frac{S^2 + (N - M)^2 p^2}{(L + N - 2M)^2 + (R + S)^2}\right\}^{\frac{1}{2}} \cos(pt + \epsilon) = A\cos(pt + \epsilon), \text{ say}$$

$$y = \left\{\frac{R^2 + (L - M)^2 p^2}{(L + N - 2M)^2 + (R + S)^2}\right\}^{\frac{1}{2}} \cos(pt + \epsilon') = B\cos(pt + \epsilon'),$$

$$\tan\epsilon = \frac{p\,\{R(N - M) - S(L - M)\}}{S(R + S) + (L + N - 2M)(N - M)p^2},$$

$$\tan\epsilon' = -\frac{p\,\{R(N - M) - S(L - M)\}}{R(R + S) + (L + N - 2M)(L - M)p^2}.$$

A and B are the maximum currents in the two branches ACB, ADB respectively, and

$$\frac{A}{B} = \sqrt{\frac{S^2 + (N - M)^2 p^2}{R^2 + (L - M)^2 p^2}}.$$

If the circuits be so adjusted that A = B

$$R^2 + (L - M)^2 p^2 = S^2 + (N - M)^2 p^2,$$

and

$$p^2 = \frac{R^2 - S^2}{N^2 - L^2 - 2M(N - L)}.$$

The value of the impedance $\sqrt{R^2 + p^2L^2}$ is nearly independent of R for rapid frequencies in ordinary copper wire circuits

Suppose

$$n = 10^6, \qquad p = 2\pi \,.\, 10^6, \qquad \text{and} \qquad L = 10^4,$$

then

$$p^2L^2 = 4\pi^2 \,.\, 10^{20}.$$

If the value of R for the particular period was 2 ohms say, then

$$\frac{R^2}{p^2L^2} = \frac{1}{100\pi^2}$$

a very small quantity.

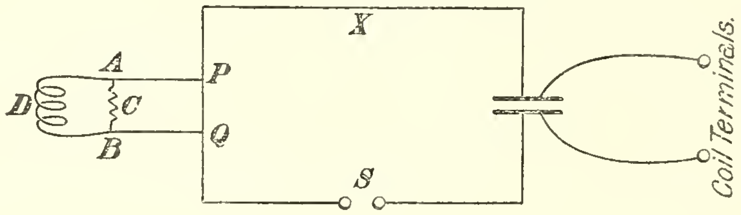
We therefore see that, under ordinary circumstances, the resistances may be neglected in comparison with the inductances.

If the branch ACB of the divided circuit consist of a high resistance of short length, and consequently small inductance, and the other branch of an inductance N, and the maximum values of the currents in the two branches are equal, then $p^2 = \frac{R^2}{N^2 - L^2}$, since S^2 may be neglected in comparison with R^2, and supposing the value of M to be small compared with N.

If the inductances are unchanged, $N^2 - L^2$ is practically a constant for all periods, and p is therefore proportional to R.

In practice, one branch of the divided circuit consisted of a standard inductance, N, and the other branch of an electrolytic resistance, R. The equality of currents in the two circuits was obtained by altering the value of R until the effect on the detector needles was the same for both circuits. Since the effect on the needle was the same in both circuits, the maximum values of the current are the same, since each branch is traversed by an oscillation of the same period.

Fig. 4.



It was not found necessary to place the divided circuit in series with the discharge circuit, but the arrangement was more satisfactory when it was shunted off a portion, PQ, of the discharge circuit XPQS (fig. 6), whose period is to be determined. The addition of the shunt circuit had no appreciable effect on the period of the oscillation for the equivalent inductance of the two branches QP, QBAP, was slightly less than that of QP, and the length of QP was generally not a tenth part of the whole discharge circuit.

ACB, ADB are the branches of the divided circuit. In C was placed a resistance consisting of zinc sulphate with zinc electrodes. The amount of resistance in the current could be varied by altering the length of electrolyte through which the current passed.

In D was placed a standard inductance consisting of six turns of insulated wire wound on a bobbin 10 centims. in diameter. The self-inductance of this could be accurately determined by calculation, and was very approximately the same for steady as for rapidly changing fields.

If the inductance L of the resistance branch was small compared with N, the value of p is given by $p = R/N$.

Even if $L = \frac{N}{10}$ the correction would only be 1 per cent. The resistance R of the zinc sulphate solution was determined for steady currents, and it can be shown that the change of resistance due to the concentration of the currents on the surface is quite inappreciable for the periods investigated on account of the high specific resistance of the solution.

This can experimentally be shown as follows: a tube containing the solution to be tested is placed inside a solenoid of a few turns, and a detector needle placed in the solution. After the passage of a discharge it will be found that the effect on the needle is the same as when the solution is removed, showing that there is no screening action on the needle due to the solution. Since the law of decrease of magnetic force from the surface inwards is the same as for the decrease of amplitude of a current through the conductor, it follows that the amplitude of the current at the centre of the solution was the same as at the surface, and that there was no alteration of the resistance of the electrolyte due to concentration of the current on the surface.

An air condenser of calculable capacity C was discharged through a circuit whose inductance L for rapid frequencies could be very approximately determined.

The value of $p = \frac{1}{\sqrt{LC}}$ obtained from theory was found to agree to within 3 per cent. of the experimentally-determined value, and, from the difficulty of accurately calculating the inductance, it is probable that the experimental determination is nearer the true value.

From the close agreement of theory and experiment, we have indirectly proved that the resistance of an electrolyte like zinc sulphate is the same for high frequencies as for low.

As an example of the determination of the period of oscillation, the value of N, the standard inductance, was 6500 units. When the current was the same in both circuits, the value of R was 168 ohms.

Therefore

$$p = \frac{R}{N} = \frac{168 \cdot 10^9}{6500} = 2 \cdot 6\ 10^7.$$

The frequency $n = p/2\pi = 4 \cdot 1\ 10^6$.

The value of the capacity and the inductance for rapid frequencies of the discharge circuit could also be determined.

If a Leyden jar of unknown capacity C be replaced by an air condenser of known capacity C′, the value of L remaining unaltered, and the value of the resistance necessary for equality of currents in the two circuits determined as before, then if p' and R′ be the new values of p and R,

$$p = \frac{1}{\sqrt{LC}} \quad \text{and} \quad p' = \frac{1}{\sqrt{LC'}},$$

$$R = pN \quad \text{and} \quad R' = p'N.$$

Therefore

$$\frac{C}{C'} = \frac{p'^2}{p^2} = \frac{R'^2}{R^2}.$$

Since R and R′ have both been determined, C is known in terms of the standard capacity C′.

Similarly, the value of L, the self-inductance for rapid frequencies, may also be found. If an additional standard inductance L′ be introduced into the circuit, the value of the capacity remaining unaltered,

$$p = \frac{1}{\sqrt{LC}} \quad \text{and} \quad p' = \frac{1}{\sqrt{(L + L')C}}.$$

Therefore

$$\frac{L + L'}{L} = \frac{p^2}{p'^2} = \frac{R^2}{R'^2}.$$

The value of L for rapid frequencies is thus determined in terms of L′, a known inductance.

In the experiments on the determination of periods, a detector consisting of twenty or more fine insulated steel wires, about 1 centim. long, was used, with one or two turns of wire round it through which the oscillatory current passed. This small detector coil was fixed before a magnetometer, and was so arranged that it could be switched either into the resistance or inductance branch of the divided circuit.

The inductance of the detector coil was too small to appreciably alter the distribution of the current in either circuit. The equality of currents in the two circuits could thus be readily compared.

The "longitudinal" detector may also be used for rough determinations; but it is not so sensitive to slight changes of current as the solenoidal detector of fine wire.

It was found that the inductance of a current when the wire was of iron was nearly the same as when replaced by copper of the same diameter. It was difficult to determine the variation of inductance accurately in this case, in consequence of the oscillations being rapidly damped when iron wires were used.

Since the capacities of condensers for very rapid alternations may be determined, it was interesting to observe whether the values of the specific inductive capacity of glass was the same for slow as for very rapidly varying fields. Some observers had found that glass had a much lower specific inductive capacity for rapid oscillations than for slow, while others again found values about the same in the two cases. The value of the specific inductive capacity found for plate-glass was about 6·5 for periods of about 3 million per second. This is considerably higher than the value obtained for plate-glass by J. J. Thomson and Blondlot, who found values of 2·7 and 2·3 respectively for periods of about 20 million per second.

The value of the specific inductive capacity of ebonite, tested by the same method, was found to be about the same as for slow alternations.

These experiments were performed in the Cavendish Laboratory, Cambridge.

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II. *Complete Freezing-Point Curves of Binary Alloys containing Silver or Copper together with another Metal.*

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Section I.

This paper contains some results of a study of the freezing points of binary alloys, the freezing points being traced for all proportions of the two metals, so that the results when plotted give a complete freezing-point curve.

The freezing point, properly speaking, is the temperature at which a liquid and some solid that can be formed from it are in equilibrium. In practice, at all events when working with alloys, it is necessary to take as the freezing point the temperature at which solid matter begins to separate from a liquid that is being slowly cooled. The first indication of this formation of solid is generally afforded by a thermometer immersed in the liquid, the heat given out when solid matter separates arresting the fall in temperature and causing the thermometer to register a constant temperature for a shorter or longer time. It is evident that, except when we are dealing with a pure substance, the freezing point obtained in this way must be below the true freezing point. This cause of error can be diminished by using a sensitive thermometer, by using a large mass of substance, and by causing the rate of fall to be very slow.* Surfusion also, where it occurs, must be prevented by the usual method of dropping in nuclei. When the freezing point changes a good deal for a small change in the concentration, this method is liable to give values of the freezing point considerably below the true value.

The general theory of the equilibrium between a liquid mixture of two bodies and the various solids that can be formed from such a mixture, has been developed by Le Chatelier, Van't Hoff, Bakhuis Roozeboom, Küster, and other writers, and it will be convenient to give here a brief outline of that part of their conclusions which we shall afterwards need.

The solid which separates when a homogeneous liquid mixture of two bodies is cooled may consist of either of the two substances, or it may be a compound formed from them; it may also in certain cases be a solid solution, or it may be an isomorphous mixture of the two bodies, or of a compound with one of them.

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* See note, Section IV.

To take the simplest case first. Let us suppose that the pure substance A separates in the solid form when we cool the homogeneous liquid AB.* If θ is the equilibrium temperature (the freezing point) reckoned from the thermo-dynamic zero, x the molecular concentration of A in the liquid AB, that is, the fraction of a molecular weight of A contained in every molecular weight in AB, λ the latent heat of solution of a molecular weight of A in AB at the equilibrium temperature, then it is known that these quantities are connected by the equation

$$2 \cdot \frac{dx}{x} = \frac{\lambda}{\theta^2} \, d\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

When x is near unity, that is, when but little of B is present, we may fairly take λ to be the latent heat of fusion of A, and θ and $d\theta$ being known by experiment, we may use equation (1) either to deduce x and therefore the molecular condition of B from the known value of λ, or following the reverse order we may obtain λ on some assumption as to the molecular state of B. This course has been largely followed in the study of solutions in water and in organic solvents, but the method has not, so far as we know, been applied to the study of metals of high melting point except by ourselves.

A great and valuable extension of equation (1) is due, we believe, to LE CHATELIER. He assumes, as a first approximation, that λ is independent of x and of θ, and he is thus able to integrate the equation, obtaining

$$2 \log_e x = \lambda \left(\frac{1}{\theta_0} - \frac{1}{\theta} \right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2),$$

where θ_0 is the freezing point of pure A, corresponding to the concentration $x = 1$.

If now we plot as abscissæ the values of x from 1 to 0, and as ordinates the corresponding values of θ calculated from equation (2), we get the ideal freezing-point curve of A. The corresponding curve for B can be plotted in the same way, but from right to left.

The highest point of each curve gives the melting point of the pure substance; and the intersection of the two curves (see fig. 1) gives, as OSTWALD has pointed out, an approximation to the melting point and composition of the eutectic alloy. The freezing-point curves found by experiment will resemble fig. 1, but on account of many causes, which may be summed up as changes in the value of λ, cannot be expected to be identical with it. In fig. 4, we give ideal curves for silver and copper, using in equation (2) the values of λ found by us. If we use PERSON'S value of the latent heat of silver, the two curves will be found to intersect at a composition very near that of the eutectic alloy. The intersection of the experimental curves in the eutectic point terminates the part of each curve which is generally realizable, although by utilizing phenomena of selective surfusion, both LE CHATELIER* and DAHMS† consider that they have, in one or two cases, traced the lower branches for a short distance.

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* By the symbol AB we mean, not a compound of A and B, but any mixture of the two bodies.

In a certain sense the phenomenon of the eutectic state gives rise to a horizontal branch of the freezing-point curve, passing through the eutectic point E, fig. 1; for if we take a mixture represented by the point X and allow it to cool, the changes in its state will be represented by points on the vertical XYZ. There will be a freezing point at Y followed by a slow fall in temperature until the temperature Z is reached, when the part *still liquid* will have the composition of the eutectic state E, and will solidify without further fall in temperature, thus giving a second very well marked freezing point. This phenomenon of double freezing points has long been known, and is well shown in the silver-copper curve given in this paper.

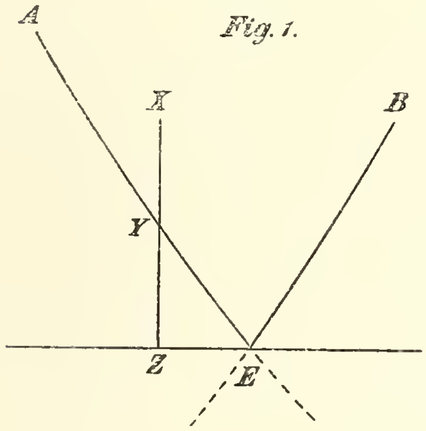
Fig. 1.

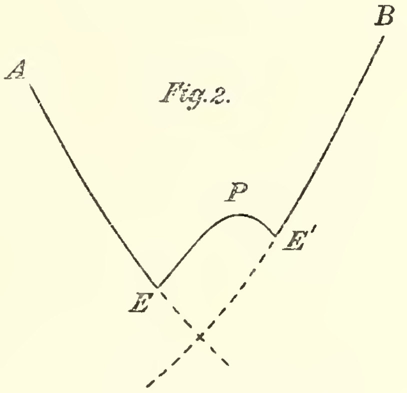
Fig. 2.

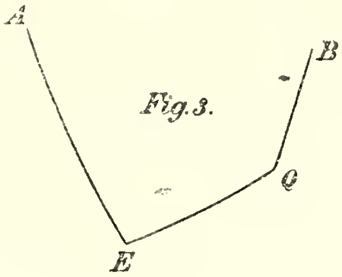
Fig. 3.

Let us now suppose that a compound C of A and B exists, whose composition and melting point in the pure state are given by the point P. Then, if P lies above the curve of fig. 1, and C is not completely dissociated by melting, we shall get a freezing-point curve such as fig. 2, with two eutectic points E and E′. This sort of curve is well illustrated by the copper-aluminium curve given by LE CHATELIER ('Revue Générale des Sciences,' 30 June, 1895), and in the work of ROOZEBOOM on the equilibrium between water, hydrochloric acid, and ferric chloride ('Zeitsch. Phys. Chem.,' vol. 15, p. 588). If more than one compound is possible, the main curves of fig. 1 may be interrupted by more than one such middle curve.

If the compound C is not at all dissociated by melting, then P may be an angle and will divide the figure into the two complete systems AC and CB, each corresponding to the case of fig. 1, and obeying the equations discussed above; but the more C is dissociated the more rounded will be the point P, and the less conspicuous the "middle" curve, of which it is the summit. Attention has been drawn to this by LORENTZ and STORTENBECKER ('Zeitsch. Phys. Chem.,' vol. 10, p. 194). If C is wholly dissociated by fusion, we should not expect its existence to be indicated by the freezing-point curve; and as LE CHATELIER has pointed out, if its melting point* lies below the curve of fig. 1, the existence of the compound may equally fail to appear in the freezing-point curve. We believe that such cases of partial dissociation on fusion are probable in the case of alloys (see 'Jour. Chem. Soc.,' 1891, p. 936, and 1894, p. 65).

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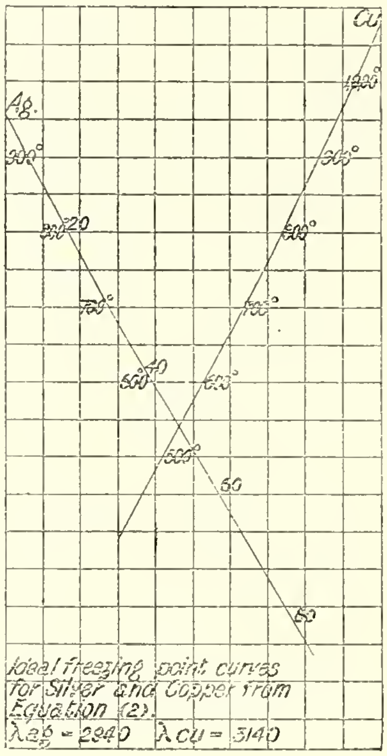
* 'Comptes Rendus,' April 9, 1894.

† 'Ann. Phys. Chem.,' 1895, vol. 54, 386.

Fig. 4.



In fig. 3 we have a case of probably frequent occurrence, where P, the melting point of C, lies below the curve B, but a portion of the system CA is possible, as shown by the curve QE. Both LE CHATELIER and ROOZEBOOM give examples of this, and some of the curves occurring in this paper probably contain examples of the same phenomenon.

Thus an intermediate maximum indicates a compound and gives its composition, while an angle such as Q may *indicate* a compound, but does not necessarily give its composition.

If, instead of one of the pure bodies A or B, or a compound, the substance formed is a "solid solution," in VAN'T HOFF's sense of the word, we should expect the line of freezing points starting from the point A to rise, or at all events the fall in the

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[*] In such a case the compound decomposes into a solid and a liquid part; as when the deca-hydrate of sodium sulphate "melts" in the presence of a saturated solution of the salt.

freezing point caused by the presence of B to be less than the normal. It is not quite certain that the experiments described in the present paper contain any examples supporting Van't Hoff's theory of solid solutions.

On the other hand, the fact proved experimentally by Küster and by Le Chatelier, that when the solid separating is an isomorphous mixture of A and B, all the freezing points lie on a straight line joining A to B, is probably illustrated by part of the copper-tin curve.

When the liquid AB separates into two conjugate liquids before the formation of solid, this process, which, since it generally occurs with falling temperature, may be expected to be exothermic, might evolve enough heat to affect the thermometer and give a false freezing point. The freezing point curve of a pair of conjugate liquids in contact with each other is perfectly illustrated by our copper-lead curve.

Section II.

The Experimental Method.

The experimental details of our work, including the method of employing and standardising the pyrometers, has been fully described in a paper already published by us;* we shall, therefore, treat these matters with great brevity.

The composition of each alloy was determined synthetically: a weighed amount of one metal being melted, and successive weighed quantities of the second metal added to it. Each freezing point was in general determined twice, the alloy being completely re-melted before the second reading. When the two differed, the second was generally a little higher than the first, and was accepted as the most trustworthy.

The alloys were fused in cylindrical salamander (plumbago) crucibles, 42 millims. wide and 105 millims. high; these were in most cases surrounded by an outer crucible, to secure a slow rate of cooling. The crucibles were heated in a small Fletcher blast furnace, so arranged that the products of combustion escaped at the side. The oblique hole, usually seen in the cover of these furnaces, was replaced by an axial circular hole that exactly fitted the crucible. The mouth of the crucible passed through this hole, and the joint was made approximately gas-tight by a packing of asbestos paper. The surface of the alloy was in this way protected against the furnace gases. As there was thus no draught across the mouth of the crucible, we were able to keep a small flame of coal-gas, or hydrogen, constantly burning over the surface of the metal. This was introduced into the crucible through a pipe-stem, and effectually prevented the oxidation of the metals or the absorption of oxygen by the silver. The hydrogen was made by the action of sulphuric acid on zinc free from arsenic, but we did not find that the substitution of coal-gas altered the freezing point. For all temperatures above the melting point of silver, the coal-gas, burning in the crucible with an insufficient supply of air, deposited so much carbon that the crucible soon became full; we were therefore obliged to employ hydrogen in such cases.

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* 'Chem Soc. Jour.,' 1895, p. 160.

Before and during the reading of the freezing point the metal was stirred by means of a plunging stirrer. This stirrer consisted of a carbon rod screwed into a semi-annular foot cut from a plate of gas-carbon so as nearly to fit the crucible. Without efficient stirring it is impossible to obtain sharp and consistent readings of the freezing point when the solutions are at all concentrated. The stirring was in some cases effected automatically by means of a small water motor, but more often hand stirring was adopted. Hand stirring, though not so vigorous as an automatic stir, has the advantage that the person stirring can note the formation of precipitate and observe its character.

The pyrometers employed were of the CALLENDAR-GRIFFITHS type, in which the temperature is determined by the change in the electrical resistance of a platinum wire. Their constants were re-determined from time to time during the progress of the experiments, using as fixed points, ice, steam, and the vapour of boiling sulphur (444·53°). These three points are sufficient for reducing, by CALLENDAR'S rule, the observed resistance to the temperature on the Centigrade-air scale. The justification for this rule is to be found in CALLENDAR'S[*] comparison with the air thermometer up to 600° C., and in the identity of the freezing point of copper, as determined by us and by HOLBORN and WIEN,[†] the latter observers virtually using the air thermometer. This point has also been discussed by GRIFFITHS.[‡] The exact accuracy of this reduction to the Centigrade-air scale is not, however, of moment for the purpose of the present paper; it is sufficient that these pyrometers give consistent temperatures on a scale that nowhere differs much from the true scale. The additional experience gained in making the experiments described in the present paper has confirmed us in the opinion that such is the case.

SECTION III.

The Tables of Experimental Results.

Each table gives the freezing points for a pair of metals. The weight of pure metal that we start with is given at the head of the table or section.

Column (1) gives the total weight of the second metal present at the moment of taking the freezing point.

Column (2) gives the percentage of the second metal present in the alloy. The percentage of the first metal present can be obtained by subtracting the numbers of column (2) from 100.

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[*] CALLENDAR, 'Phil. Trans.,' A., 1887, p. 161; A., 1891, p. 119.

[†] HOLBORN and WIEN, 'Ann. Phys. Chem.,' 1892, **47**, 107.

[‡] GRIFFITHS, 'Nature,' November 14, 1895, and February 27, 1896.

Column (3), the *Atomic Percentage* of the second metal, gives the number of atoms of the second metal in every 100 atoms of the alloy. It would be more satisfactory if we could calculate the number of molecules of the second metal in every 100 molecules of the alloy, but unfortunately we can only make uncertain guesses as to the molecular weights. As before, by subtracting the number in column (3) from 100 we get the atomic percentage of the first metal. Columns (2) and (3) are not calculated beyond the second decimal place, as this gives a degree of accuracy equal to that of the freezing points in column (4).

Column (4) gives the freezing point. This temperature was read to one-hundredth of a degree, but in the tables we, as a rule, only give the tenths of a degree.

Column (5), the *Atomic Fall*, is obtained by dividing the total depression of the freezing point, taken from column (4), by the atomic percentage taken from column (3). This column shows how far the law of proportionality between the concentration and the total depression of the freezing point holds good. For concentrated solutions the atomic fall has no simple meaning, and in such cases it is not given in the tables. In applying equation (1) to the case of dilute solutions, for which alone the conception of the atomic fall is useful, we must regard dx as identical with $1 - x$. This is the atomic percentage divided by 100, so that the atomic fall is $\frac{1}{100} \cdot d\theta/dx$, a quantity which equation (1) tells us is equal to $\cdot 02\theta^2/x\lambda$. If we use the more accurate equation (2), then the atomic fall is $\frac{\theta \, . \, \theta_0}{\lambda(1-x)} \cdot 02 \log_e x$. The two expressions become identical when x is unity.

Numbers in column (4), which are enclosed in brackets, are *second* freezing points, corresponding to a eutectic state.

Each series in a table corresponds to an entirely new alloy, and the horizontal spaces dividing a series into sections indicate that a portion of the alloy has been extracted from the crucible and the experiments continued with the residue.* It will be seen that the freezing point was always taken *after* as well as *before* such an extraction.

The notes and remarks at the end of each table are substantially copied from the laboratory note-book.

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* Table IIA contains examples of this.

TABLE IA.—Freezing Points of Alloys formed by adding Copper to Silver.

Series 1.—348·9 *grams Silver.*

(1.) Total weight of copper present	(2.) Percentage weight of copper.	(3.) Atomic percentage of copper.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	960·0	
1·074	·31	·52	957·2	5·4
2·101	·60	1·02	954·3	5·6
4·195	1·19	2·01	948·7	5·6
8·11	2·27	3·81	938·6	5·61
13·59	3·75	6·23	925·3	5·57
24·03	6·44	10·50	902·4	5·49
44·87	11·39	17·99	864·9	5·28

Series 2.—200 *grams Silver.*

(1.) Total weight of copper present	(2.) Percentage weight of copper.	(3.) Atomic percentage of copper.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	959·3	
7·305	3·52	5·86	926·1	5·66
22·35	10·05	16·00	865.3	5·88
32·86	14·11	21·88	847·3	5·12
43·57	17·88	27·08	825·3	4·95
55·67	21·77	32·18	805·0	4·80
61·74	23·59	34·48	797·0	4·71
"	"	"	(778·0)	
67·95	25·36	36·67	788·9	4·65
"	"	"	(778·6)	
74·05	27·02	38·70	781·7	4·59
"	"	"	(778·6)	
78·16	28·10	40·00	778·65	
82·16	29·12	41·18	779·1	
90·34	31·12	43·50	790·3	
"	"	"	(778·6)	
103·02	34·00	46·75	805·3	
"	"	"	(778·2)	
118·38	37·19	50·22	818·80	

Series 1.—Before adding the last quantity of copper the galvanometer was balanced, and it was observed that at the moment after the addition of the copper there was no sudden change of temperature. The total weight of the metals used in this series was 393·8 grams, but the ingot of alloy was found to weigh 379 grams. Although some of the alloy adhered to the crucible and to the pyrometer stem, and hence was not weighed, yet these numbers point to a probable loss of metal during the course of the experiments. The metal was molten for periods amounting to about five hours in all.

Series 2.—The first two freezing points of the alloy in this series prove, when plotted, to be inconsistent with the results of the other series and with the later points of this series. A probable explanation is that the silver was not fully molten at the moment of adding the first and second quantities of copper, and so the solution, whose freezing point was taken, was at the time richer in copper than the figures indicate.

At 16 atoms, precipitate begins to form at the freezing point and can be watched forming freely as the mass slowly falls in temperature.

At 34·48 atoms, a second lower freezing point, much more constant in temperature than the upper point, was noted. This is reached when the still liquid portion attains the composition of the eutectic alloy—40 atoms of copper. This freezing point, and all other similar eutectic points, *have the temperature placed in brackets*, to distinguish it from the upper first freezing point at which solid *begins* to separate. This eutectic point is probably the same whatever the proportions of copper and silver. When an alloy by partial solidification reaches this temperature, the thermometer no longer falls slowly as solidification progresses, but registers a quite constant temperature. until the whole mass is solid.

The total weight of the metals used in this series was 318·4 grams, but the ingot of alloy was found to weigh 315 grams, and a little was left on the stirrer.

At 32·18 atoms there was a trace of surfusion.

TABLE IA.—Freezing Points of Alloys made by adding Copper to Silver.

Series 3.—182·57 *grams Silver.*

(1.) Total weight of copper present.	(2.) Percentage of copper.	(3.) Atomic percentage of copper.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
8·739	4·57	7·55	917·0	5·70*
17·447	8·72	14·01	883·7	5·44
18·65	9·27	14·83	880·0	5·39†
19·99	9·87	15·73	875·4	5·38
21·41	10·50	16·67	870·7	5·36
23·03	11·20	17·70	866·0	5·31
24·74	11·93	18·77	861·1	5·27
26·54	12·69	19·86	856·3	5·22
28·24	13·40	20·87	851·8	5·18
30·25	14·22	22·03	846·7	5·14
33·25	15·41	23·70	839·5	5·08
39·66	17·85	27·03	825·5	4·98‡

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[*] As usual, at this stage, there was an abundant precipitate at and after the moment of reading, and a few degrees below the recorded freezing point stirring became impossible.

[†] Here the period of stationary temperature was very short.

[‡] In most of the above experiments there was an abundant precipitate at the moment of reading the temperature, but the freezing point, though quite marked, was not constant for long.

These experiments, when plotted, show that there is no inflexion in the curve on the silver side.

The ingot of alloy weighed 220·5 grams, while the metals used weighed 222·2 grams.

At the first three readings of this series surfusion was noticed.

TABLE IB.—Freezing Points of Alloys made by adding Silver to Copper.

Series 1.—200 *grams Copper.*

(1.) Total weight of silver present.	(2.) Percentage of silver.	(3.) Atomic percentage of silver.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	1081·5	..
1·023	·51	·30	1079·1	8·0*
4·374	2·14	1·27	1071·1	8·2
9·532	4·55	2·72	1059·1	8·24
14·84	6·91	4·17	1048·1	8·01
29·85	12·99	8·05	1019·6	7·69
,,	,,	,,	1020·8	7·54†
45·06	18·39	11·67	996·5	7·28
60·07	23·10	14·98	976·0	7·04
80·34	28·66	19·07	953·5	6·71
100·54	33·45	22·77	934·4	6·46
120·68	37·64	26·15	917·4	6·28‡

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* When the silver was dropped into the molten copper it appeared to boil.

† Up to this point coal-gas had been used to protect the surface of the copper from oxidation, but so much finely divided gas carbon had formed in the crucible that pure dry hydrogen was henceforward used. The gas carbon does not form over molten silver at its melting point. This reading was taken two days after the preceding.

‡ The weight of the metals used was 320·7 grams, but the ingot, after dipping while hot in dilute sulphuric acid, weighed 310·4 grams. The surface of the ingot was mottled with white spots on a ground of copper colour.

TABLE IB.—Freezing Points of Alloys made by adding Silver to Copper.

Series 2.—124·73 grams Copper.

(1.) Total weight of silver present.	(2.) Percentage of silver.	(3.) Atomic percentage of silver.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
75·27	37·64	26·15	916·5	6·31*
90·43	42·03	29·84	900·2	6·08
110·58	47·00	34·22	881·6	5·84
130·60	51·16	38·06	866·5	5·65
150·70	54·72	41·48	852·9	
175·86	58·51	45·27	837·2	
,,	,,	,,	(778·4)	†
200·94	61·71	48·59	823·7	
,,	,,	,,	(778·6)	‡

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* Series 2 begins where Series 1 ends. The difference of ·9° C. between the last reading of Series 1 and the first reading of Series 2 is perhaps a measure of the changes in composition that the mixture of Series 1 has undergone by volatilization and oxidation. If so, these two causes of error, when taken together, are not very important. A shift in the constants of the pyrometer during Series 1 might well amount to as much as 1° C.

† Partial stirring was possible until the temperature fell to the eutectic point

‡ The ingot of alloy weighed 319 grams instead of the 325·6 grams of metal used, but several fragments of alloy adhering to the apparatus were not weighed, so that the loss from all causes was small during the experiments.

Table Ic.—Freezing Points of the Eutectic Alloy of Silver and Copper.

200 *grams Silver.*

(1.) Total weight of copper present.	(2.) Percentage of copper.	(3.) Atomic percentage of copper.	(4.) Freezing point on the Centigrade scale.
72	26·47	38·03	783·44
"	"	"	(777·15)
74·05	27·02	38·70	780·4
76·04	27·55	39·33	(777·25)
"	"	"	779·11
77·80	28·01	39·87	777·59
79·11	28·34	40·27	777·76
82·13	29·11	41·18	780·45
"	"	"	781·49
"	"	"	778·55
87·15	30·35	42·63	787·09
"	"	"	778·45

The ingot of alloy weighed 286·5 grams, while the total weight of the metals used was 287·15.

At temperatures but little above the eutectic, the stationary temperature at the F.P.* lasted but a short time, so that there was some danger of reading these freezing points too low; to meet this, nuclei of alloy were extracted from the crucible and dropped in just before the temperature fell to the freezing point. This method removes the risk of surfusion and slightly raises the observed F.P.

There was an interval of a night between the earlier readings of this series and the last four, but the constants of the pyrometer were not re-determined. A change in the constants may be the cause of the fact that the first F.P. on the second day was a degree higher than the F.P. of the same alloy on the previous day. We have, therefore, in drawing the curve of this series subtracted one degree from all the second day's readings.

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* F.P. is "freezing point."

TABLE IIA.—Freezing Points of Alloys made by adding Lead to Silver.

200 *grams Silver.*

(1.) Total weight of lead present.	(2.) Percentage of lead.	(3.) Atomic percentage of lead.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	959·12	
2·004	0·99	·52	954·34	9·2
4·004	1·96	1·03	949·0	9·8
6·005	2·92	1·54	944·0	9·8
10·005	4·76	2·54	934·4	9·72
14·335	6·69	3·61	924·3	9·67
"	"	"	924·5	*
20·335	9·23	5·04	910·4	9·67
30·335	13·17	7·33	886·6	9·89
45·335	18·48	10·57	853·4	10·00
60·34	23·18	13·60	820·0	10·23
80·34	28·66	17·32	782·7	10·19
105·34	34·50	21·56	741·6	
130·34	39·46	25·37	710·0	
160·33	44·50	29·49	684·1	
200·34	50·04	34·32	659·5	
		134·84 *grams Silver.*		
135·07	50·04	34·32	659·2	†
175·07	56·49	40·38	635·4	
215·07	61·47	45·42	619·3	
"	"	"	(308·5)	
255·07	65·42	49·66	606·2	
295·07	68·63	53·30	596·1	
		77·7 *grams Silver.*		
170·00	68·63	53·30	596·3	‡
210·00	73·00	58·51	580·8	
255·00	76·64	63·12	563·0	
315·00	80·22	67·90	548·3	

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* The second freezing point was taken on the resumption of the experiment after a night's interval.

† Residue of the above alloy after the removal of 130·4 grams; the freezing point was taken after a night's interval.

‡ Residue after the removal of 182·2 grams.

For the first 5 atomic per cents. of lead there was an abundant precipitate at the moment of reading. After this concentration the precipitate at the moment of reading gradually became less and less, and before 45 atomic per cents. it ceased to be possible to detect precipitate at the moment of reading or for some time afterwards. At this concentration plenty of precipitate could be felt on the bottom of the crucible when the alloy had cooled 50 or 100 degrees below the F.P.

At 45 atomic per cents. of lead the alloy was allowed to cool to the eutectic point, but stirring had become impossible long before the temperature had fallen to this point.

Beyond 50 atomic per cents. of lead the F.P. is only indicated by a slight decrease in the rate of cooling.

At 34·32 atomic per cents. and at 53·3 atomic per cents. the crucible had become too full and a portion of the alloy was removed. It will be noticed that the F.P. before and after this removal of a part of the alloy is substantially the same.

At the end of the experiments the solidified ingot of alloy was found to weigh 389·8 grams, while from the weights of the two metals used it should have weighed 392·7 grams; part of this loss is due to metal adhering to the pyrometer and the crucible.

Oxidation did not occur either during the experiments or during the cooling.

TABLE IIB.—Freezing Points of Alloys made by adding Silver to Lead.

250 *grams of Lead.*

(1.) Total weight of silver present.	(2.) Percentage of silver.	(3.) Atomic percentage of silver.	(4.) Freezing point on the Centigrade scale.
0	0	0	327·60
5·216	2·04	3·85	306·17
,,	,,	,,	(303·72)
10·431	4·01	7·41	(303·5)
,,	,,	,,	(303·2)
15·647	5·89	10·71	(303·2)
20·862	7·70	13·80	(303·4)
26·078	9·45	16·67	460·6
31·293	11·13	19·36	481·6
39·116	13·53	23·08	505·5
46·94	15·81	26·47	523·6
54·76	17 97	29·58	536·9

The second reading at 7·41 atoms was taken on the day after the first. Until 16·67 atomic per cents. of silver no higher point than the eutectic could be found although the alloys were heated above 500° C., and the cooling carefully watched until the eutectic point was reached. This must be due to the fact that very little solid separates out at the F.P. With more than this proportion of silver the F.C. could be detected, but the indication was slight until 23 atomic per cents. of silver.

The eutectic point deduced from the above is 303·3°; in our previous work ('Chem. Soc. Jour.,' 1892), using mercury thermometers, we made it 303°, the fixed points on the mercury thermometers having been previously determined by comparison with a platinum thermometer.

TABLE IIIA.—Freezing Points of Alloys made by adding Tin to Silver

200 *grams Silver.*

(1.) Total weight of tin present.	(2.) Percentage of tin.	(3.) Atomic percentage of tin.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	959·2	
1·013	·504	·461	956·1	6·72
2·891	1·425	1·304	950·0	7·06
6·926	3·347	3·067	936·3	7·47
11·172	5·290	4·856	921·8	7·70
19·39	8·839	8·139	891·0	8·38
33·51	14·350	13·28	830·2	9·69
48·63	19·57	18·18	755·9	11·18
63·87	24·20	22·59	691·7	11·84
		201 *grams Silver.*		
78·89	28·19	26·40	648·2	11·78
98·92	32·98	31·02	603·1	11·47
119·65	37·32	35·23	567·4	11·12
		137·82 *grams Silver.*		
82·04	37·32	35·23	567·6	*
97·43	41·42	39·24	538·7	
117·51	46·02	43·79	510·2	
137·69	49·98	47·72	489·2	
157·96	53·41	51·16	474·0	
179·44	56·56	54·34	464·1	
,,	,,	,,	(220·2)	
		91·94 *grams Silver.*		
119·73	56·57	54·34	463·0	†
135·53	59·59	57·38	453·3	
161·11	63·67	61·55	437·9	
188·25	67·19	65·17	424·8	
		68·35 *grams Silver.*		
139·97	67·19	65·17	425·0	‡
160·34	70·11	68·19	413·0	
190·42	73·59	71·80	399·2	
230·89	77·16	75·51	381·4	
,,	,,	,,	(221·4)	

* Residue of the preceding alloy after the removal of 100·8 grams.

† ,, ,, ,, ,, ,, 105·6 ,,

‡ ,, ,, ,, ,, ,, 71·9 ,,

For the first five atomic per cents. at least, the moment of freezing is detected by the person stirring a second or two before the observer at the galvanometer, as the walls of the crucible become abundantly coated with a smooth solid.

At 22 atomic per cents. nuclei of silver were added just before the reading, but no effect was noticed, and the nuclei of silver did not melt easily.

At 35·23 atomic per cents., and at a temperature considerably above the F.P., some of the alloy was extracted.

At the higher freezing point at 54·34 atomic per cents., and for 50° or more below the F.P., no solid could be detected, but the reading was well-marked. The lower F.P. was obtained by allowing the alloy to cool to the eutectic state.

A portion of the alloy was now removed; the F.P. afterwards was a degree lower.

At 65·17 atomic per cents. a portion of the alloy was removed, the F.P. before and after this process being the same.

At and after 54 atomic per cents., little or no solid matter can be detected at the point recorded as the F.P., but the cooling at this point suddenly becomes much slower.

At 75·5 atomic per cents. no solid matter could be detected until close to the eutectic point. Soon after this point was reached the alloy set to a solid mass at the eutectic temperature.

Table IIIb.—Freezing Points of Alloys made by adding Silver to Tin.

180 *grams Tin.*

(1.) Total weight of silver present.	(2.) Percentage of silver.	(3.) Atomic percentage of silver.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	232·07	
3·289	1·80	1·96	226·54	2·82
6·579	3·53	3·85	221·67	
8·224	4·37	4·76	(221·59)	
"	"	"	232·5	
11·513	6·01	6·54	259·5	
18·092	9·13	9·91	296·9	
24·67	12·05	13·04	322·6	
36·18	16·74	18·04	355·2	
49·34	21·52	23·08	380·8	

It is clear that the eutectic state is reached with somewhat less than 3·85 atomic per cents. of silver.

The readings, higher than the eutectic, until 10 atomic per cents. of silver, are very fugitive, the F.P. being indicated by a slight change in the rate of cooling. One would expect these readings to be subject to a large experimental error, but the curve shows that they are consistent with each other.

It will be noticed that where the two series meet the latter lies some five degrees higher. The discrepancy may be due to some small extent to a change in the constants of the pyrometer, to a greater extent to an error in the determination of the last F.P. of the first series, but we think it is also due in part to a loss of silver by volatilization and splashing during the course of the first series.

TABLE IVA.—Freezing Points of Alloys made by adding Lead to Copper.

Series 1.—200 *grams Copper.*

(1.) Total weight of lead present.	(2.) Percentage of lead.	(3.) Atomic percentage of lead.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	1080·8	
1·00	·50	·15	1079·3	10·0
2·122	1·05	·32	1077·1	11·6
5·124	2·50	·78	1071·6	11·8
10·124	4·82	1·55	1062·8	11·6
15·124	7·03	2·26	1055·1	11·37
25·12	11·16	3·70	1039·2	11·25
40·12	16·71	5·78	1018·3	10·81
60·12	23·11	8·42	995·0	10·19
80·12	28·60	10·92	977·6	9·45
105·12	34·45	13·86	963·6	8·46
135·12	40·32	17·13	954·4	
155·12	43·68	19·18	953·3	
175·12	46·68	21·13	953·1	
195·12	49·38	22·99	953·1	
215·12	51·82	24·76	953·2	
Series 2.—96 *grams Copper.*				
104	52·01	24·90	951·1	
164	63·08	34·33	952·3	
254	72·58	44·73	952·0	
394	80·41	55·67	951·2	
424	81·54	57·47	950·8	

TABLE IVB.—Freezing Points of Alloys made by adding Copper to Lead.

Series 1.—250 *grams Lead.*

(1.) Total weight of copper present.	(2.) Percentage of copper.	(3.) Atomic percentage of copper.	(4.) Freezing point on the Centigrade scale.
0	0	0	327·6
1·765	·70	2·26	327·2
4·965	1·95	6·10	327·6
24·29	8·86	24·10	917·0
26·44	9·57	25·70	924·0
29·44	10·54	27·80	932·2
34·46	12·12	31·06	941·1
37·58	13·07	32·94	945·1
41·81	14·33	35·35	948·8
46·83	15·78	37·97	952·6
51·98	17·21	40·47	953·3
”	”	”	326·9
57·21	18·63	42·80	953·7
67 39	21·23	46·85	954·5

Series 2.—400 *grams Lead.*

0	0	0	327·3
2·45	·61	1·97	326·0
21·96	5·20	15·24	858·1
30·04	6·99	19·70	890·8

The following numbers refer to the atomic percentage of lead in table IV.

At ·15 the stirrer set fast soon after the reading of the F.P.

At ·32 there was much precipitate at or just after the reading, but stirring was possible.

At 2·26 a very liquid substance was left on the surface after the bulk had precipitated, or been beaten down by the stirrer to the bottom of crucible.

At 8·4, after the F.P., a solid forms on the top, but it can be beaten down to the bottom of the crucible, until most of the alloy is solid, with some quite liquid at the top.

At 17·13 no precipitate was felt for some time after the F.P.

From 19·18 to quite 50 the temperature at the F.P. is, for some minutes, very constant, like that of a eutectic mixture. There is no perceptible precipitate at the F.P. or for some time after, and then it is noticed adhering as a layer to the walls of the crucible.

From 50 to 60 the temperature, though quite constant at the F.P., did not remain constant for so long a time as before.

From 60 to 85, the last point that could be observed, the halt in the fall of temperature at the F.P. became rapidly less marked, that at 80 and 85 being very transient.

Repeated efforts were made to determine the F.P. of mixtures containing more than 85 atomic percentages of lead, but the only stop in the cooling takes place at 327°·5, the F.P. of pure lead, or more strictly the F.P. of a eutectic mixture of copper and lead. It will be seen that, at 60 atomic percentages of lead, the eutectic point was 327°. In this series of experiments we did not attempt to make a minute study of the eutectic alloy of copper and lead; but on a previous occasion, using a sensitive mercury thermometer ('Chem. Soc. Journ.,' 1892, p. 906), we found that copper lowered the F.P. of lead by 1°·17 C., and that the eutectic alloy contained rather less than ·2 atomic percentage of copper.

The difficulty of tracing the upper branch of the curve between 85 and 100 atomic percentages of lead is not due to the insolubility of copper in lead, for, at a red heat, copper dissolves freely; but rather to the fact that, between these limits, the solubility changes but little with change of temperature, so that at any given temperature the amount of solid that separates is small. It is evident that the curve must become almost vertical for dilute solutions.

At the end of each series, after removing the pyrometer and stirrer, the furnace was closed as completely as possible, and the alloy allowed to cool slowly in a current of reducing gas. When cold, the alloys were weighed. They were in the form of cylinders, 3 centims. wide and from 4 to 7 centims. long. Each ingot was completely covered with a thin layer of soft metal, which appeared to be almost pure lead, but, on cutting a plane face from end to end along the cylinder, the character of the alloy could be studied.

At 24·76 atomic percentages of lead the alloy was found to weigh 413 grains, instead of 415, which is the sum of the weights of the metals used. During the earlier experiments with this alloy, a few particles had been splashed out of the crucible. The alloy appeared quite free from oxide.

The structure revealed by the face cut on the cylinder was as follows:—two or three millims. at the top were lead-coloured, with a few spots of copper that were invisible to the naked eye, but could be seen by the aid of a lens. Below this, for 4·5 centims., the metal was copper-coloured, but the lens, or indeed a careful inspection with the naked eye, showed a great number of irregular roundish spots of lead-coloured metal embedded in the mother substance. The bottom centimetre consisted of grey metal which, to the naked eye, presented a well-marked tinge of red from the large number of spots of copper scattered through it. The lines separating the middle copper layer from the upper and lower layers were perfectly sharp to the naked eye; the upper boundary line was convex, the lower boundary quite straight.

At 54·47 atomic per cents. of lead the ingot weighed 519 grams, while the sum of the weights of the metals used was 520 grams.

The face cut on this ingot showed that the upper layer of lead-coloured metal was so thin as to be barely visible. The copper coloured layer had more grey in it, and was only 5 millims. deep. Its line of separation from the lower lead-coloured layer was somewhat irregular. This grey layer formed the bulk of the alloy, being 6 centims. long.

As before, it had a reddish tinge from the spots of copper scattered through it. These were uniformly distributed, except near the top, where complete separation had not occurred. The copper tinge was less pronounced than at 24·76.

At 53·15 atomic per cents. of lead the ingot weighed 312·5, while the total weights of the two metals come to 317·4.

As might be expected, this strongly resembled the preceding alloy, except that it was less homogeneous, cavities being visible, especially in the lead part, containing octahedral crystals of copper.

At 80·3 atomic per cents. of lead the alloy weighed 427 grams instead of 430. This alloy was homogeneous to the eye, being lead-coloured throughout. In some lights the upper 2 centimetres had the faintest reddish tinge, but this detail was uncertain. Only a very few minute specks of copper could be detected even by careful examination with a lens. There were no cavities in the alloy.

It will be noted, by comparison with fig. 9, that while the first three ingots which show separation into two layers correspond in composition to points on the flat part of the curve, the fourth ingot, which is homogeneous, corresponds to a point on the descending portion of the curve.

Table V.—Freezing Points of Alloys made by adding Bismuth to Copper.

250 *grams Copper.*

(1.) Total weight of bismuth present.	(2.) Percentage of bismuth.	(3.) Atomic percentage of bismuth.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	1077·2	
2·354	·933	·286	1074·0	11·2
7·161	2·79	·87	1067·2	11·5
12·626	4·81	1·51	1059·9	11·46
18·656	6·94	2·22	1052·9	10·94
28·793	10·33	3·39	1041·3	10·59
40·295	13 88	4·68	1029·7	10·15
55·762	18·24	6·36	1014·9	9·79
76·55	23·44	8·52	999·1	9·17

Table VI.—Freezing Points of Alloys made by adding Gold to Copper.

250 *grams Copper.*

(1.) Total weight of gold present.	(2.) Percentage of gold.	(3.) Atomic percentage of gold.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	1079·70	
1·120	0·45	·144	1079·56	1·00
4·336	1·71	·554	1076·95	4·96
10·524	4·04	1·333	1072·08	5·72
16·936	6·30	2·129	1067·88	5·55
26·787	9·68	3·325	1060·61	5·74

TABLE VIIA.—Freezing Points of Alloys made by adding Tin to Copper.

Series 1.—200 *grams Electrolytic Copper.*

(1.) Total weight of tin present.	(2.) Percentage of tin.	(3.) Atomic percentage of tin.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	1082·1	10·4
1·855	·92	·50	1076·9	11·3
5·549	2·70	1·47	1065·5	11·98
12·062	5·69	3·13	1044·6	13·44
24·152	10·78	6·08	1000·4	
45·192	18·43	10·80	909·6	
71·16	26·24	16·02	788·8	
86·20	30·12	18·77	757·7	
96·40	32·53	20·53	742·0	
„	„	„	742·0*	
101·49	33·66	21·39	738·8	
112·04	35·91	23·10	734·3	
119·96	37·50	24·32	730·8	
123·61	38·20	24·88	729·0	
126·66	38.77	25·35	727·4	
131·67	39·70	26·09	724·5	
137·73	40·79	26·96	720·7	
120·28 *grams Copper.*				
82·84	40·79	26·97	220·6†	
88·05	42·27	28·18	714·9	
98·55	45·03	30·51	702·8	
118·57	49·65	34·57	680·0	
143·88	54·47	39·07	655·1	
173·91	59·12	43·67	633·1	
204·51	62·97	47·68	615·7	
74·56 *grams Copper.*				
126·73	62·97	47·68	616·0‡	
157·00	67·81	53·03	593·8	
187·47	71·55	57·41	576·1	
249·05	76·97	64·17	546·7	

The first three freezing points of this series were well marked, and accompanied by a considerable formation of precipitate.

At 16 atoms of tin the freezing point was a very steady temperature, and there was much precipitate at the moment of reading.

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* Determined the day after the previous reading.

† Residue of the preceding alloy after the removal of 134·6 grams.

‡ „ „ „ „ „ 123·5 „

The freezing points from 20·53 to 24·32 inclusive were noted as being so steady as to resemble eutectic points. This is the region from $SnCu_4$ to $SnCu_3$.

At 24·32 atoms no precipitate was noticed at the moment of reading the freezing point, but before the metal had cooled two degrees below the recorded temperature stirring had become impossible; in fact, this alloy may be said to solidify at a constant temperature.

At 25·35 atoms, that is, with more tin than corresponds to $SnCu_3$, we begin again to notice an abundant precipitate at the moment of reading the freezing point.

After the first reading at 26·96 atoms of tin a portion of the alloy was removed from the crucible. This alloy was white, hard, and brittle, with a conchoidal fracture.

At 30·51 atoms the freezing point was not so well marked as hitherto. There was much precipitate soon after the reading.

At 34·57 atoms of tin surfusion was noticed at the freezing point.

From here onwards, as we add more tin, the pause in the cooling, which marks the freezing point, becomes less and less marked, but up to 64·2 atoms of tin there is no difficulty in determining the freezing point. There is now no precipitate observed at the moment of reading the freezing point, or for some time afterwards.

Table VIIa.—Freezing Points of Alloy made by adding Tin to Copper.

Series 2.—200 *grams Electrolytic Copper.*

(1.) Total weight of tin present.	(2.) Percentage of tin.	(3.) Atomic percentage of tin.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	1081·0	
6·046	2·93	1·954	1062·3	11·73
37·07	15·64	9·04	944·8	15·07
67·08	25·12	15·24	797·9	A
,,	,,	,,	793·1	B
83·16	29·37	18·23	762·8	

The points A and B are two well-marked freezing points of the same alloy, the lower temperature B corresponding to some eutectic state (see Curves).

For the purpose of drawing the curve, in order to bring this series into agreement with Series 1, one degree was added to the first reading given above, and proportional amounts to the lower readings.

TABLE VIIA.—Freezing Points of Alloys made by adding Tin to Copper.

Series 3.—147·6 *grams Copper.*

(1.) Total weight of tin present.	(2.) Percentage of tin.	(3.) Atomic percentage of tin.	(4.) Freezing point on the Centigrade scale.
52·40	26·20	15·99	789·2*
56·42	27·66	17·01	777·9*
61·42	29·39	18·24	763·9
66·43	31·04	19·45	750·1
68·27	31·63	19·87	745·4 A
,,	,,	,,	742·7 B
68·77	31·79	19·99	744·6
69·27	31·94	20·11	743·8
70·29	32·26	20·34	742·5
78·63	34·76	22·22	736·1
86·96	37·08	24·00	731·1
91·47	38·26	24·94	728·1
95·97	39·40	25·85	724·9
100·48	40·51	26·74	721·1

Up to 20 atomic per cents. of tin there was abundant precipitate just at or after the reading of the freezing point.

After 20 atomic per cents. of tin the readings became very steady.

The freezing points A and B are for the same alloy. They indicate different phenomena.

TABLE VIIA.—Freezing Points of Alloys made by adding Tin to Copper.

Series 4.—200 *grams Copper.*

(1.) Total weight of tin present.	(2.) Percentage of tin.	(3.) Atomic percentage of tin.	(4.) Freezing point on the Centigrade scale.
0	0	0	1083·9
41·46	17·17	10	928·9
54·05	21·28	12·65	867·5
58·80	22·72	13·61	845·0
62·81	23·90	14·41	825·5
65·81	24·76	15·00	809·4 A
,,	,,	,,	794·3 B
68·81	25·60	15·57	795·0
71·89	26·44	16·15	788·4
82·07	29·10	18·03	767·5
87·30	30·39	18·96	756·7 C
,,	,,	,,	745·8 D

* Surfusion was noticed.

From 10 to 13·61 atoms of tin, inclusive, it was noticed that a soft precipitate began to form on the walls of the crucible at the moment of reading the freezing point and rapidly increased.

At 12·65 atoms the freezing point was indicated, not by a period of stationary temperature, but by a sudden marked decrease in the rate of cooling.

At 14·41 atoms, in spite of copious precipitate, stirring was quite easy for several degrees below the freezing point. This point was distinctly indicated.

At 15 atoms, readings A and B, different freezing points for the same alloy, correspond to different phenomena. At A there was little precipitate; B was a much steadier temperature, with abundant precipitate of a finely gritty character. At this moment the alloy felt to the stirrer like a mixture of sand and water.

The reading at 15·57 atoms, or just below it, resembled B.

From 16·15 atoms onwards the freezing points are very steady temperatures, quite different in character from the preceding, except B.

C and D correspond to different phenomena, D being so constant as to resemble a eutectic point. At D the alloy sets to a solid mass without a further fall in temperature.

TABLE VIIB.—Freezing Points of Alloys made by adding Copper to Tin.

200 *grams Tin.*

(1.) Total weight of copper present.	(2.) Percentage of copper.	(3.) Atomic percentage of copper.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	232·32	
1·006	·50	·93	229·69	2·93
1·854	·92	1·70	(227·78)	
5·029	2·45	4·48	(227·77)	
,,	,,	,,	262·60	
10·50	4·99	8·92	364·4	
21·32	9·63	16·39	433·1	
36·82	15·55	25·57	496·3	
46·85	18·98	30·42	521·2	

The freezing point of the pure tin was marked by surfusion.

The atomic fall for copper in tin, 2·93°, is identical with that obtained by us in 1889 with a mercury thermometer ('Chem. Soc. Jour.,' 1890, p. 392).

The readings at 1·7 and 4·48 atoms of copper give the freezing point of the eutectic alloy of tin and copper.

The freezing points on the rising branch of the curve up to 16·39 atoms, and to a lesser degree up to 30·42 atoms, are very difficult to observe and are liable to a large experimental error. No solid matter can be detected for some time after the freezing point.

TABLE VIIc.—Freezing Points of Copper-Tin Alloys.

Double Points.

(1.) Total weight of metals present.	(2.) Percentage of tin.	(3.) Atomic percentage of tin.	(4.) Freezing point on the Centigrade scale.
Cu 200, Sn 87·3	30·39	18·96	757·00 A
„	„	„	746·5 B
Cu 202·58, Sn 87·3	30·12	18·77	746·05 B
Cu 212·72, Sn 87·3	29·10	18·04	768·0 A
„	„	„	745·8 B
Cu 300·72, Sn 87·3	22·50	13·47	848·4 C
„	„	„	795·3 D

At the points marked A there was much fine sandy precipitate soon after reading, which rapidly increased until the mass was nearly solid, but not set, as the stirrer could still be moved a little. At the points marked B the stirrer set fast, before the reading the mass was really solid. The reading C was fugitive whilst the reading at D was very steady.

In charting, these temperatures were all reduced by the subtraction of 1·5° to obtain agreement with Series 1. A comparison with Series 4 will show the justice of this correction.

Series VIIc. was carried out six months after the others, and with a different pyrometer.

Table VIIIa.—Freezing Points of Alloys made by adding Antimony to Silver.

200 *grams Silver.*

(1.) Total weight of antimony present.	(2.) Percentage of antimony.	(3.) Atomic percentage of antimony.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	958·8	
1·089	·542	·486	954·6	8·64
2·758	1·361	1·222	947·8	9·00
5·987	2·907	2·615	934·3	9·37
12·16	5·732	5·173	906·9	10·03
22·39	10·068	9·124	853·6	11·53
41·40	17·15	15·66	734·3	14·33
63·52	24·10	22·17	608·3	15·81
73·92	26·99	24·91	561·5	15·95
84·59	29·72	27·50	545·2	
89·75	30·98	28·71	539·1	
95·23	32·26	29·93	532·5	
106·97	34·85	32·43	520·7	
118·49	37·21	34·70	510·7	
		126·39 *grams Silver.*		
74·88	37·21	34·70	511·5*	
86·00	40·49	37·90	499·1	
97·18	43·47	40·83	488·9	
117·72	48·23	45·53	493·4	
,,	,,	,,	(485·0)	
,,	,,	,,	(485·4)†	
128·31	50·38	47·67	496·8	
158·80	55·69	52·99	509·6	

Up to 40·83 atomic per cents. of antimony the pure metal from tartar emetic was used, beyond this concentration the commercial antimony was used.

Up to 2·6 atomic per cents. the temperature at the F.P. was very steady.

Up to 10 per cents. abundant precipitate was noticed at the moment of freezing. At 15·66 there was but little precipitate noticed at the freezing point, but the person stirring could detect a change at the moment when the pyrometer indicated the freezing point. At 22·17 no precipitate was noticed at the freezing point. At 24·91 a little precipitate was noticed.

At 27·5 there was a copious precipitate at the freezing point. The temperature at the freezing point remained constant for some time, and 20° lower the alloy seemed to set to a solid mass.

From 27·5 onwards the temperatures at the F.P. are very constant to the end of the series at 53 atoms of antimony, the eutectic F.P., 485° C., having its usual character of complete constancy.

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* Residue of the preceding alloy after removal of 117·2 grams.

† Freezing point, taken on the resumption of the experiments next day.

At the end of the experiments the alloy was weighed and found to be 270 grams, while from the statement of the weights of antimony and silver used, the weight should have been 285 grams. Some of this loss is due to metal adhering to the pyrometer, stirrer, and crucible, but the missing 15 grams cannot all be accounted for thus; there has certainly been a loss of alloy by volatilization or splashing. This fact renders the atomic percentages of the latter part of the series somewhat uncertain.

TABLE VIIIB.—Freezing Points of Alloys made by adding Silver to Antimony.

200 *grams Antimony from* (*Tartar Emetic*).

(1.) Total weight of silver present.	(2.) Percentage of silver.	(3.) Atomic Percentage of silver.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	629·49	
1·05	·52	·58	627·52	3·4
2·735	1·35	1·50	624·44	3·37
6·658	3·22	3·58	617·1	3·45
12·894	6·05	6·70	607·0	3·35
33·178	14·23	15·61	581·7	3·06
64·195	24·30	26·35	555·8	2·79
69·210	25·71	27·84	552·6	
79·223	28·37	30·63	546·5	
94·708	32·14	34·54	538·6	
114·95	36·50	39·04	529·4	
135·27	40·35	42·99	521·9	
,,	,,	,,	(484·9)	
160·32	44·49	47·18	512·3	
180·39	47·42	50·13	504·9	
,,	,,	,,	(485·7)	
152·99 *grams Antimony.*				
138·00	47·42	50·13	505·6*	
158·03	50·82	53·51	497·4	
178·12	53·80	56·48	485·9	
,,	,,	,,	487·9	
188·23	55·17	57·83	486·2	
213·47	58·26	60·87	495·2	
,,	,,	,,	(485·6)†	

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* Residue of the above alloy, after the removal of 89·4 grams.

† The ingot when taken out of the crucible was bright; it weighed 360·8 grams. The calculated weight was 366·46 grams. As the loss was probably for the most part antimony, we see that there was during the experiment a loss of 2 per cent. of this metal. Splashing, spitting, and oxidation will account for this.

TABLE VIIIc.—Freezing Points of the Eutectic Mixture of Antimony and Silver

146 *grams Silver.*

(1.) Total weight of antimony present.	(2.) Percentage of antimony.	(3.) Atomic percentage of antimony.	(4.) Freezing point on the Centigrade scale.
104	41·61	39·00	(484·90)
"	"	"	493·48
104·51	41·73	39·11	(484·59)
"	"	"	493·05
106·08	42·08	39·46	(484·59)
"	"	"	491·76
108·09	42·54	39·92	490·27
"	"	"	(485·09)
111·25	43·23	40·61	488·12
"	"	"	(485·68)*
114·27	43·91	41·25	(485·68)*
"	"	"	485 98
114·97	44·06	41·41	(485·68)
"	"	"	485·99
115·98	44·27	41·62	485·71
"	"	"	485·76
119·13	44·93	42·27	485·66
124·62	46·05	43·37	489·58
133·42	47·74	45·05	493·61*
	"	"	(485·45)†

TABLE IX.—Freezing Points of Alloys made by adding Bismuth to Silver.

283 *grams Silver.*

(1.) Total weight of bismuth present.	(2.) Percentage of bismuth.	(3.) Atomic percentage of bismuth.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	958·0	
2·149	·75	·39	953·8	10·8
6·151	2·13	1·12	945·8	10·9
12 731	4·30	2·28	933·9	10·57
22·797	7·45	4·01	914·5	10·84
43·963	13·45	7·46	880·0	10·45
77·51	21·50	12·45	808·7	12·00
127·58	31·06	18·96	715·7	12·77

* Surfusion was noticed at these points.

† In this series no loss by spitting or splashing was noticed, and on account of this comparatively low temperature, little or no white smoke of oxide of antimony was observed. The alloy at the end of the experiment was found to weigh 278·45 grams, while the total weight of metal used was 279·4 grams.

At the conclusion of the experiments the alloy was weighed and found to be 404·5 grams instead of 410·6 grams, the weight of the metals used.

The weight of the silver used was not known to nearer than one gram, and this silver was slightly contaminated with nickel, and perhaps with iron.

Up to 4·01 atoms of bismuth the freezing point was marked by plenty of precipitate.

At 12·45 and 18·96 little or no precipitate was noticed at the moment of reading the freezing point, and this point was very fugitive. Some time after the freezing point, a large quantity of a fine sandy precipitate formed, and stirring was possible in this for a considerable time, the rate of cooling being very uniform.

TABLE X.—Freezing Points of Alloys made by adding Thallium to Silver.

200 *grams Silver.*

(1.) Total weight of thallium present.	(2.) Percentage of thallium.	(3.) Atomic percentage of thallium.	(4.) Freezing point on the Centigrade scale.	(5.) Atomic fall.
0	0	0	962·38	
2·639	1·30	·69	956·83	8·01
6·709	3·26	1·74	946·4	9·16
,,	,,	,,	947·1	8·77*
14·127	6·60	3·60	930·5	8·86
21·786	9·82	5·45	913·5	8·97†

SECTION IV.

Discussion of the Experimental Curves.

The curves (figs. 6–20), which embody the results of our experiments, are plotted with the temperature of the freezing point of the alloys measured vertically upwards, and the atomic percentage measured horizontally. We can hence at once get the value of the concentration x for use with equations (1) and (2). The numbers just below the line of the curve give the temperature, those just above give the atomic percentage of one metal. The individual experiments are given by the black points which lie along the course of the curve.

Dilute Solutions.

When a solution is very dilute, the observed depression of the freezing point is necessarily small, and consequently the atomic fall is liable to a large experimental error;* on the other hand, as the solution becomes more concentrated, the atomic fall changes from a number of causes that are but imperfectly understood. It is therefore somewhat difficult to decide how to take the average of a number of atomic falls. Moreover, for the strict application of equation (1) to the purpose of obtaining λ, we need the atomic fall at infinite dilution. We have attempted to get this for copper in fig. 5, by plotting the atomic percentage of dissolved metal horizontally from left to right, and the atomic fall from column (4) of the tables vertically. A line drawn through the points thus obtained and produced to cut the zero ordinate should then give the atomic fall at infinite dilution. Unfortunately, there is a good deal of uncertainty about the exact direction of the lines corresponding to each metal.

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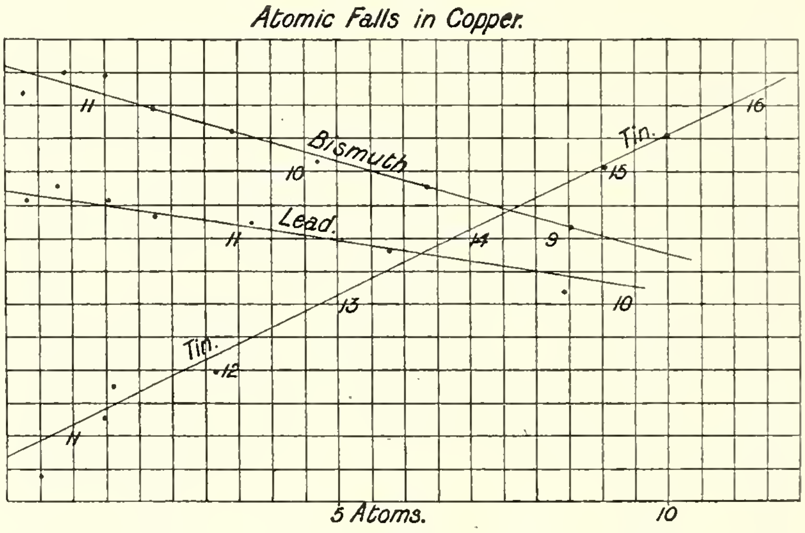
* Next day's reading.

† At the end of the experiments the alloy was found to weigh 221·2 grams; the total weight of the two metals used was 221·8 grams.

Fig. 5.



Each line corresponds to the fall in the freezing point of copper caused by the metal whose name is written above the line. The concentration is written in atoms from left to right. The atomic fall is reckoned for each metal from a different zero, but the numbers below the lines give the atomic falls in degrees Centigrade.

It will be seen that bismuth gives 11·6, lead 11·7, and tin 10·7 for this limiting value of the atomic fall. As bismuth and lead do not appear to combine with the copper, and tin evidently does so, it will be wisest to take the higher value 11·7°. Using this value in equation (1) we find that λ, the latent heat of an atomic weight of copper, is 3138 calories, the melting point being taken as 1082° C. Hence the latent heat of fusion of one gram of copper is 49·6 calories.

If instead of attempting to get the atomic falls at infinite dilution, we mean the atomic falls for concentration greater than ·5 atom and less than 2 atoms, we get, as an average from the lead and bismuth, an atomic fall of 11·6° at a concentration of 1·2 atoms. A mean of the two numbers for tin which come within these limits gives 11·5° at 1·5 atoms. These numbers used with equation (2) give a value of λ very slightly greater than the above. Hence we may say that the results of our experiments on the solution of lead, bismuth, and tin in copper lead to the value 50 calories for the latent heat of fusion of copper. We should expect this to be more probably too high than too low.

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* We have not hitherto seen a way of applying to our results a correction similar to that suggested by NERNST and ABEGG, but a modification of our method of experiment has been suggested to us that will probably enable us to do so.

The atomic fall due to gold dissolved in copper is 5·7° for a mean concentration of 2·26 atoms, using the last three values of the gold-copper table. This corresponds to a value for infinite dilution of 5·8°, which is very nearly half the above value given by lead, bismuth, and tin. Silver in copper produces a fall of about 8·2°, that is, rather more than two-thirds of the normal fall, 11·7.

The half value given by gold may mean that when in dilute solution in copper the gold molecule consists of two atoms, but it will be well to wait for further data before speculating as to the cause of these abnormally small depressions of the freezing point.

The data for the atomic fall, when silver is the solvent, are more numerous, but not on that account easier to interpret. As before, the values given by lead and bismuth are the largest; the most probable value being near 10·3°. This value leads to a latent heat of 27 calories for silver, a value considerably greater than PERSON'S value of 21. Here, also, as in the case of the copper, we must hope that further data will help us to decide whether these atomic falls really contain the key to the molecular condition of the metals in solution.

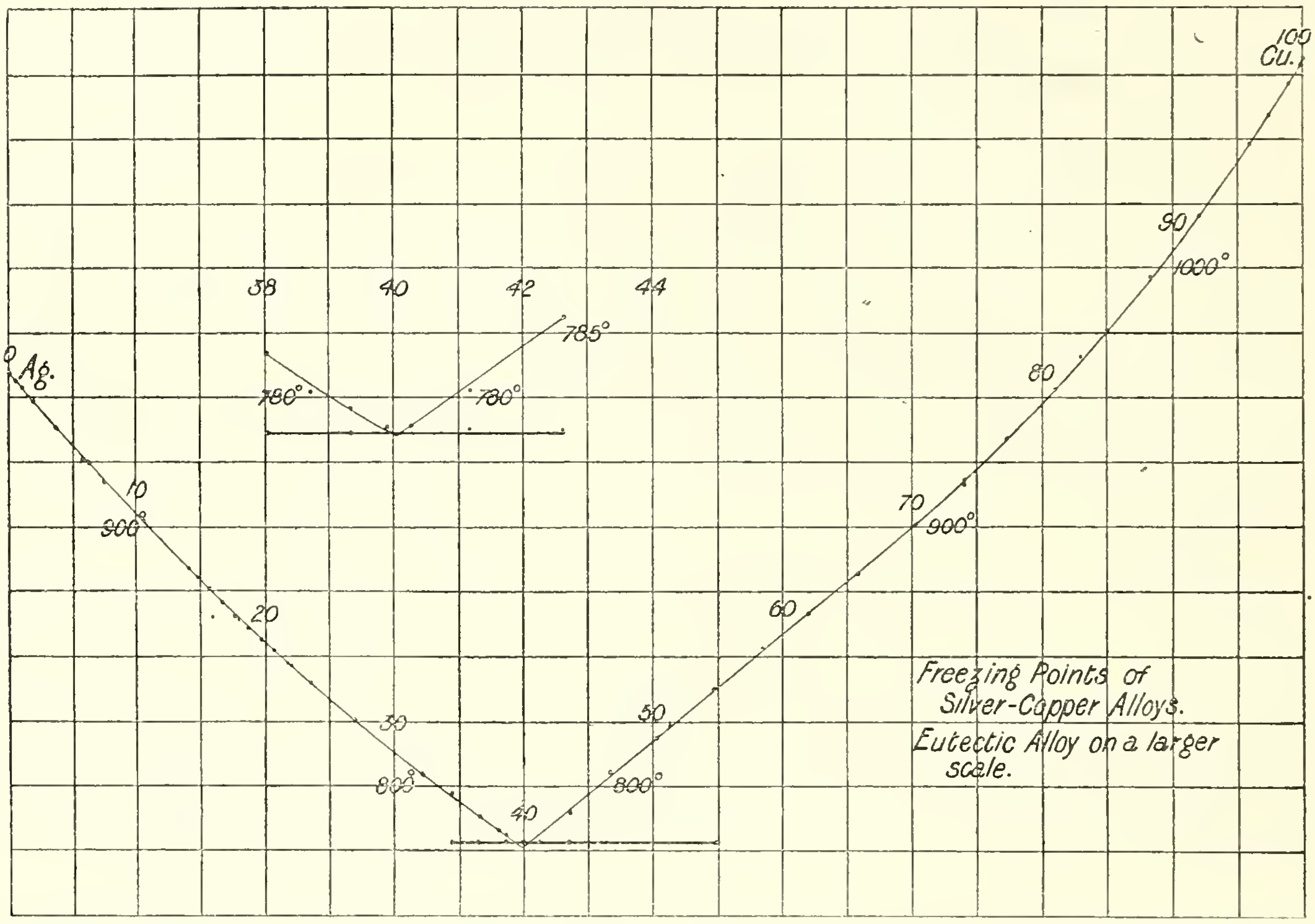
The Silver-Copper Curve. (Fig. 6.)

This, looked at as a whole, in the light of the theory of Section 1, does not at first offer a singularity or an indication of the existence of a compound; but, examined more closely, there are two points worth mention.

The first is that the depressions of the freezing point, even for very dilute solutions, are abnormally small, and the atomic falls decrease slowly in value with increasing concentration. The small depression makes it probable that the molecule of either metal, when in dilute solution in the other, is complex, consisting of more than one atom. The decrease in the atomic falls is by no means rapid, as may be seen from the slight curvature, but so far as it exists, it is an argument against the existence in the liquid alloy of molecules of a compound.

The other feature lies in the exact coincidence of the eutectic alloy, LEVOL'S alloy, with the formula Ag_3Cu_2. This struck us in our first series of experiments, but, as during a long series there is always some loss of metal, we thought it well to carry out new experiments, starting with an alloy of a composition nearly corresponding to that of the eutectic point. Table Ic. gives this series, and the results are plotted in fig. 6 above the complete curve, and on a larger scale. It is evident that this series confirms the earlier experiments, and puts the eutectic alloy exactly at Ag_3Cu_2.

Fig. 6.



The numbers below the curve give the Centigrade temperature, those above the curve give the atomic percentage of copper.

The theory of the subject, and many experiments of our own and of others, point to the conclusion that the eutectic alloy is not generally a compound, and hence should not have a formula. Some other evidence is, therefore, needed before we can accept Ag_3Cu_2 as a chemical compound.

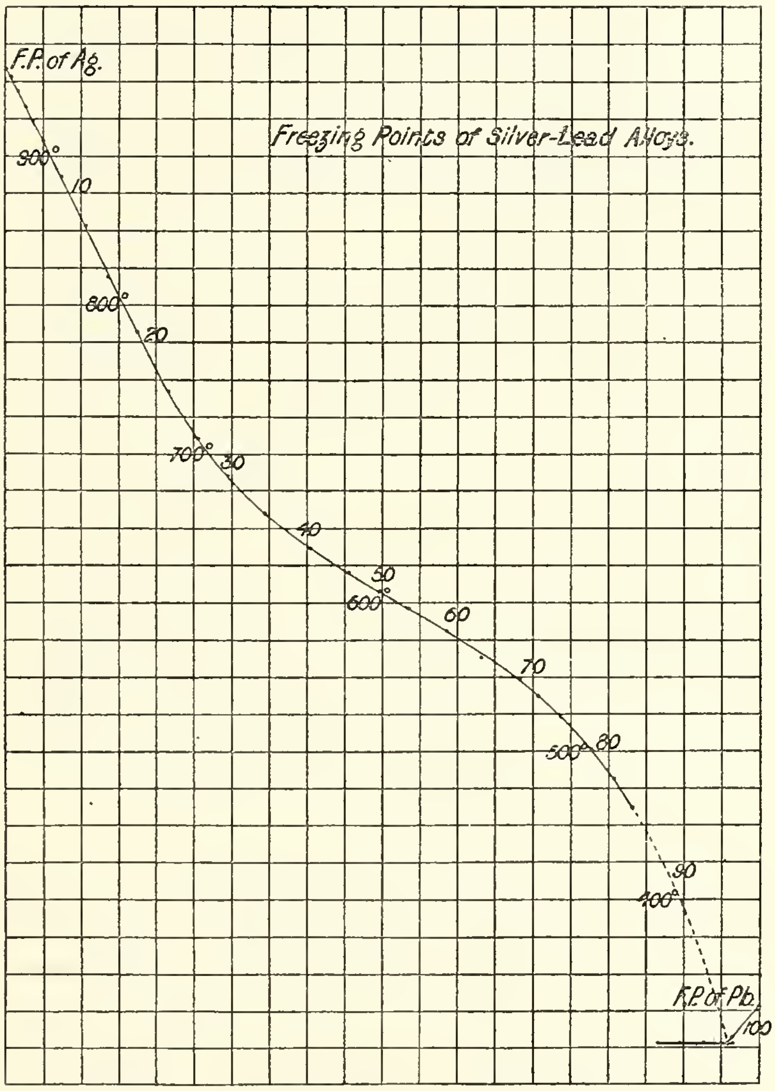
The Silver-Lead and Silver-Tin Curves. (Figs. 7 and 8.)

These two curves resemble each other strongly. Lead and tin being non-volatile and easily fusible metals, the curve consists mainly of the silver branch, although the extreme right shows the depression produced in the freezing point of lead or of tin by the addition of silver, and also the eutectic phenomenon.

The silver-lead curve is almost a straight line until 20 atoms of lead, but soon after this there begins a gradual, though marked, change in the curvature, with a point of inflexion at 50 atoms. In the tin curve the upper part is not straight, and the atomic falls increase with increasing concentration of tin in a way that suggests appropriation of the silver by the tin to form molecules of a compound. Near 50 atoms there is a point of inflexion, as in the lead curve.

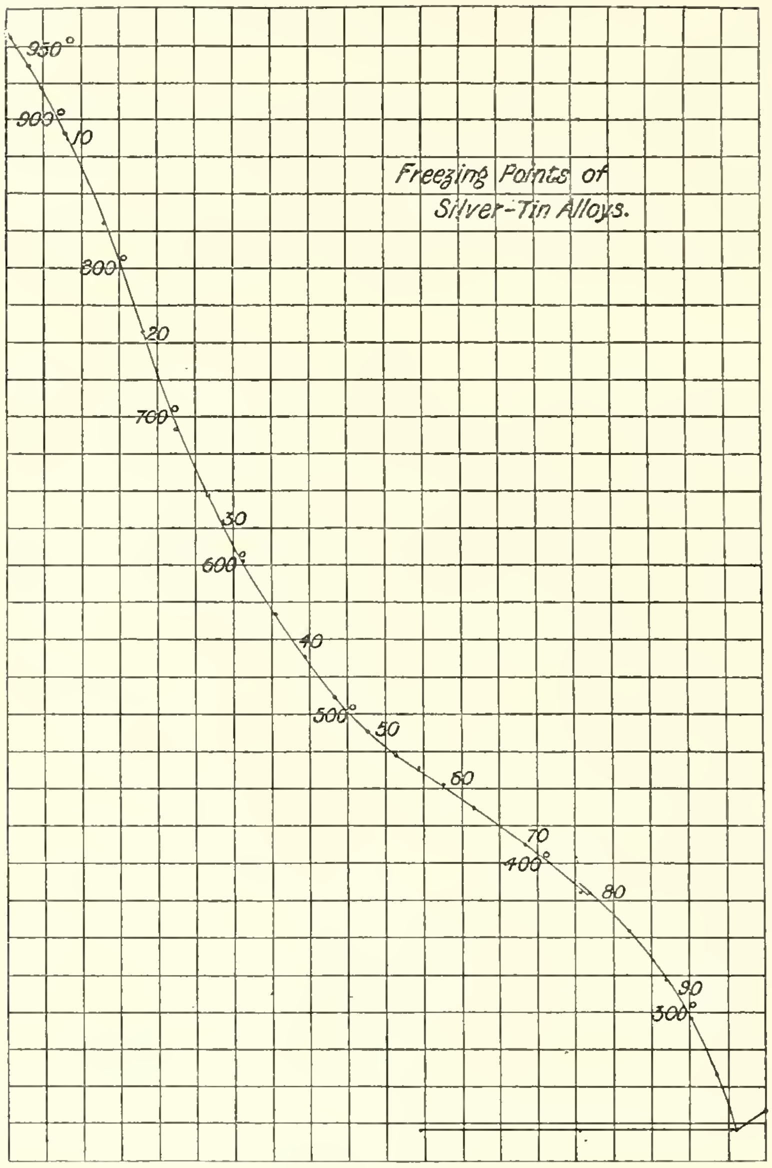
In neither curve is there an angle, until we come to the eutectic point, and from the absence of a well-marked intermediate summit it would appear that, if compounds of these metals with silver exist, they must be largely dissociated under the conditions of the experiment. The shape of the curves is, however, not inconsistent with the reality of such compounds. For example, Ag_4Pb and Ag_4Sn might well have a virtual summit below our curve at 20 atoms. But this view, though plausible, does not appear to us the most probable explanation of the curves; we are disposed to attribute the marked change in the slope, which occurs near 30 atoms in the lead curve and later in the tin curve, to the aggregation of the atoms of these metals to larger molecules, or at all events to compare the state here to the flat part of the copper-

Fig. 7.



In degrees Centigrade and atomic percentages.

Fig. 8.



In degrees Centigrade and atomic percentages.

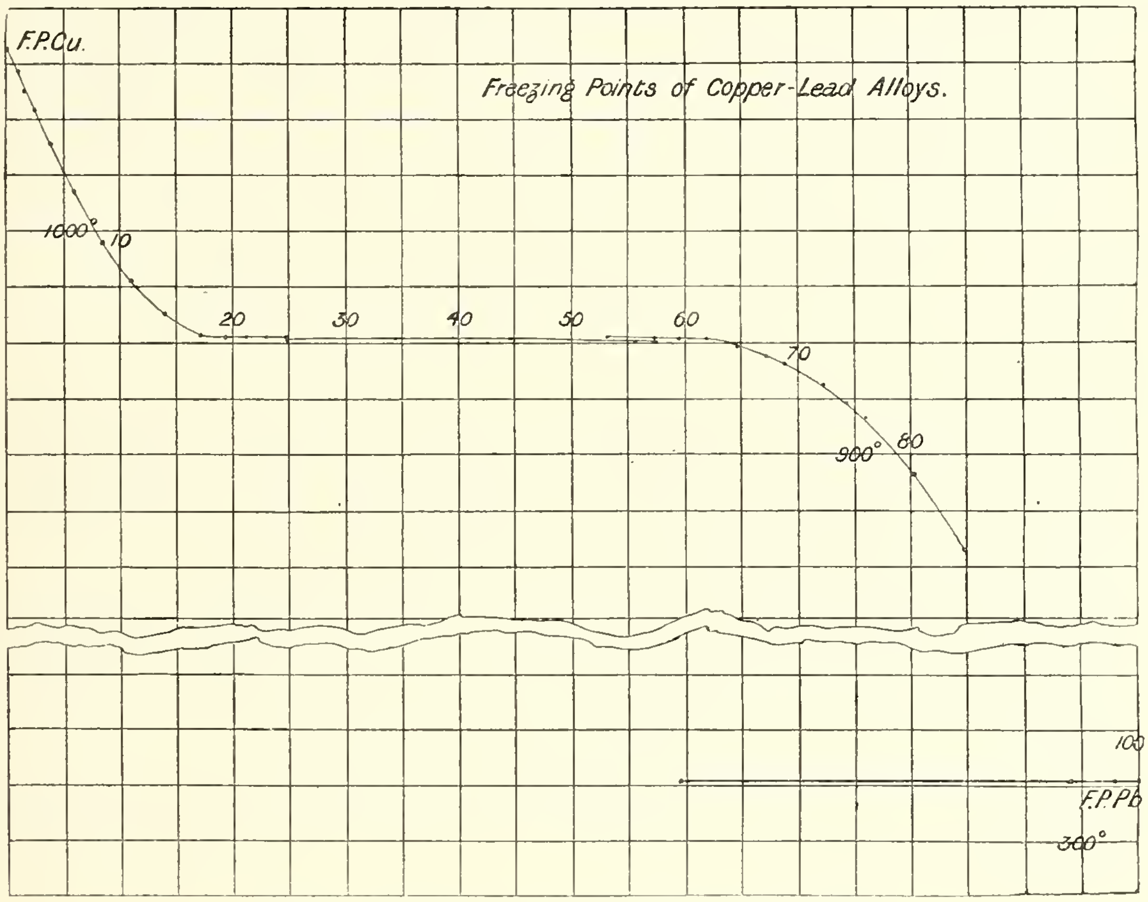
lead curve. Silver-lead and silver-tin do not probably, in our experiments, separate into conjugate liquids, but if they could be examined at a somewhat lower temperature, they perhaps would do so. These curves may be compared with the vapour-pressure curve of a mixture of water and propyl alcohol, a system which stands at the dividing line between wholly and partially miscible liquids. The portion of the silver-lead curve given as a dotted line is hypothetical, as no freezing point could be detected in this region.

The Lead-Copper Curve. (Fig. 9.)

For the first seven atoms at least of lead this curve agrees well with the ideal curve of equation (2), but as more lead is added the curve rapidly approaches the horizontal, until at 17 atoms of lead the addition of this metal ceases to affect the freezing point. From this point until 65 atoms of lead the curve is a horizontal straight line, the freezing point being constant at 954°. On this flat the freezing point of each alloy is marked by a prolonged period of constant temperature, but the character of each freezing point differs from that of a eutectic mixture, inasmuch as after a prolonged halt the temperature begins to fall again while some of the alloy is still liquid. With more than 65 atoms of lead the curve gradually droops and finally becomes nearly vertical.

The character of the solid alloys, as described in the notes to Table IV., throws a clear light on the meaning of this curve. The sloping parts of the curve correspond to the separation of solid matter from a homogeneous liquid, but for all alloys corresponding in composition to points on the flat, the liquid has separated into two conjugate liquids at some temperature above the freezing point. The composition of each of these two liquids will depend on the temperature, but provided there be more than 17, and less than 65 atomic per cents. of lead in the whole alloy, the quantity of lead present will not affect the composition of either conjugate, but only the amount of each conjugate present. Consequently all alloys between these limits are *qualitatively identical*, and therefore must freeze at the same temperature. The prolonged period of constant temperature noticed during the freezing of each alloy whose composition lies between these limits is easily explained. Let us suppose the

Fig. 9.



Degrees Centigrade and atomic per cents. of lead.

freezing point just reached, and that solid is beginning to form, as it must, from *both conjugates at once.*[*] The separation of this solid will cause one conjugate liquid to grow at the expense of the other, but the composition of each will remain the same until one conjugate has ceased to exist. Then, and then only, will the temperature begin to fall. Hence for alloys containing a good deal less than 65 atoms of lead, a large amount of solid matter will form at the freezing point, at a very constant temperature. But, as we found to be the case, the period of constant temperature observed at the freezing point of each alloy becomes shorter as the amount of lead approaches to 65 atoms.

The gradual change of curvature at both ends of the horizontal line may be due to imperfect equilibrium caused by inefficient stirring, too rapid cooling, and other causes. Or it may conceivably be due to the gradual aggregation of the lead atoms into larger masses preparatory to the separation of the alloy into conjugate liquids.

The latter part of the curve from 65 to almost 100 atoms of lead may be called the curve of solubility of copper in lead, and it ought therefore to give us by LE CHATELIER's equation (2) the latent heat of solution of copper in lead. Unfortunately this part of our curve is very steep, and therefore very difficult to determine by our method.

As we have already mentioned, very small amounts of copper produce the RAOULT effect in lead, lowering the freezing point of this metal by the normal amount corresponding to a monatomic molecule of copper (*loc. cit.*). On the flat at the lower part of the figure a eutectic point at 60 atoms will be seen.

The fact that alloys of lead and copper liquate has long been known, and the general character of the freezing-point curve of such a system could have been predicted from the work of ALEXEJEFF and KONOVALOFF, but, so far as we are aware, this is the first case that has been traced experimentally.

The bismuth-copper curve has not been carried beyond 9 atoms of bismuth, but, from an inspection of the solid alloy, we think that it will turn out to be like the lead-copper curve.

The Copper-Tin Curve. (Fig. 10.)

The lower line gives the whole curve; the upper line gives, on a large scale, the more remarkable portion, from 14 to 27 atomic per cents. of tin.

The problem of the copper-tin alloys, one of the most interesting in metallurgy, still remains obscure, in spite of the amount of work that has been done on these alloys by RICHE, BEHRENS, ROBERTS-AUSTEN, and many other writers. We fear that the results here given, though they complicate this problem, do not solve it.[†]

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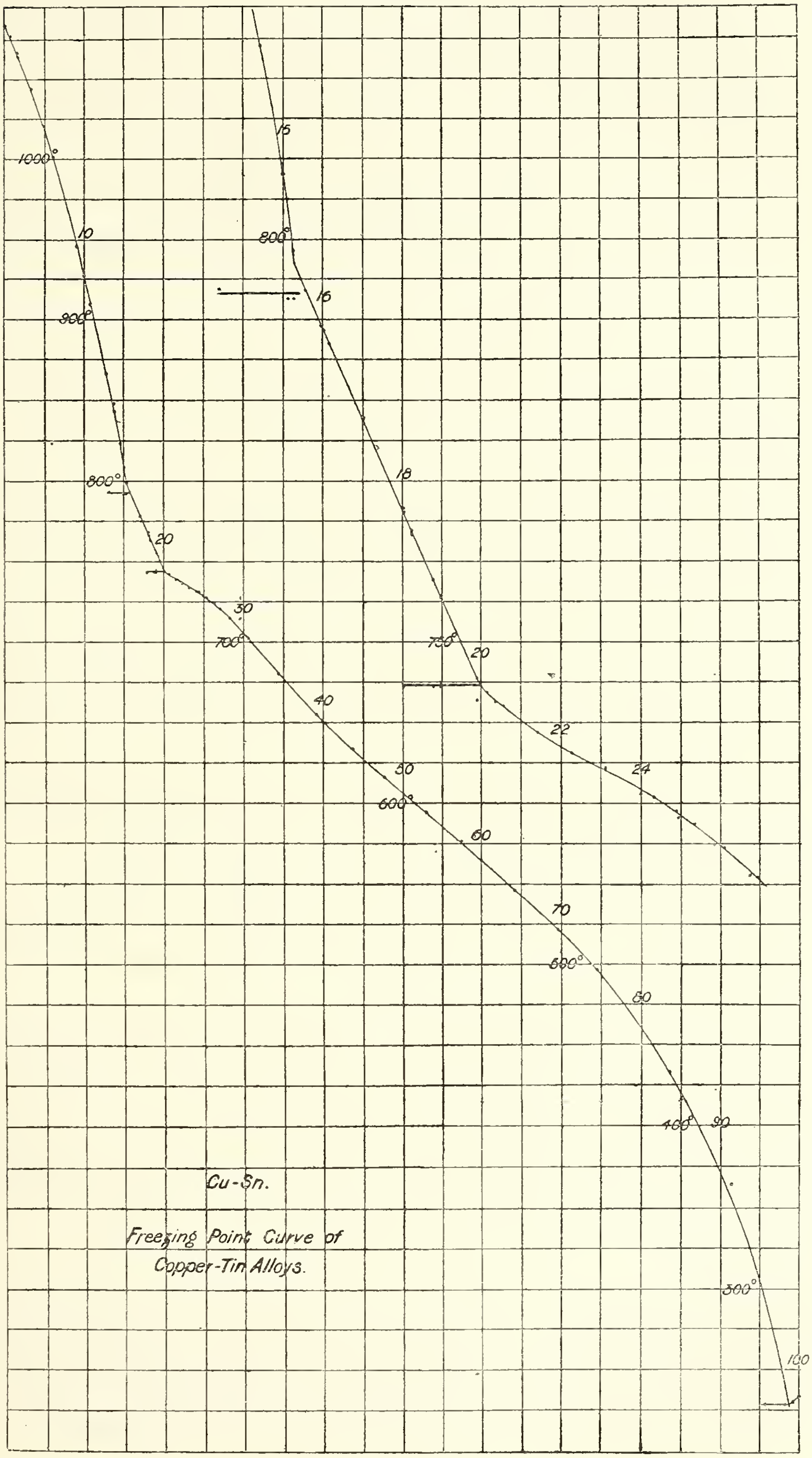
[*] Pointed out by OSTWALD.

[†] After a good deal of our work had been carried out, we found in an article on alloys by M. H. LE CHATELIER, which he was kind enough to send to us (*loc. cit.*, p. 27), a complete freezing-point curve for copper-tin. This curve agrees with ours in having an angle at $SnCu_4$, but it is on too small a scale for a comparison of other details.

Fig. 10.



The numbers below the curve give the Centigrade temperature; the numbers above the curve give the atomic percentage of tin in the alloy.

The first point that strikes one in the copper-tin curve is the rapid way in which the steepness increases with increasing percentage of tin. If we bear in mind the fact that, on account of the thermometer lag, so important where the curve is steep, the true equilibrium curve from 5 to 15 atoms of tin may lie perceptibly above our freezing-point curve, while, from the character of the freezing point at 15·5 atoms, the two curves must agree at this point, we can conclude that at 15 the true curve may be almost a vertical line. A not improbable explanation of this feature of the curve is to suppose that the tin is largely combining with the copper to form molecules, such as $SnCu_3$ or $SnCu_4$. As can be proved by the use of this assumption in equation (2), the view that the body in solution is $SnCu_3$ agrees very well with the shape of the curve up to 15 atoms of tin. But we do not attach much importance to this numerical agreement, as the assumption of the existence of molecules of $SnCu_4$, accompanied by some dissociation, would give an equally good agreement.

At 15·5 atoms of tin our curve changes its direction, and becomes a straight line; the freezing point of each alloy is now marked by a steady temperature, lasting for some time. In the figure this point appears to be a triple point, as from 13·5 atoms to 15·5 we observed two freezing points, one a slightly-marked one on the steep part of the curve, the other a very steady temperature identical with the single freezing point at 15·5. We think that the horizontal line of freezing points thus obtained represents the moment for each alloy when, through separation of solid matter at and below the upper freezing point, the still liquid portion attains the composition of 15·5 atoms.

The soft precipitate which forms at, or soon after, the freezing point on the upper branch as far as 15·2 is very unlike the abundant finely-gritty precipitate of these lower freezing points, and of the alloy as far as 18 atoms or beyond.

From 15·5 to 20 atoms the freezing point is plainly marked by a constant temperature lasting for some time; and all the points lie on a line in which we cannot see any curvature. This line ends exactly at 20 atoms, and it will be seen that we have studied this region very minutely.

Below the lower half of this line we find a horizontal line of second freezing points, causing the appearance of a triple point at, or near, 20 atoms. Each of these lower freezing points occurs after a good deal of solid matter has already formed. The alloy sets to a solid mass at the lower point, and this freezing point is marked by a period of absolutely constant temperature. We have no doubt that these lower points indicate the moment when the still liquid alloy has reached the composition of 20 atoms of tin.

From 20 to 25 atoms the curve is very nearly, but not quite, straight, and the fall in temperature caused by the increase of tin from 20 to 25 atoms is comparatively slight, being less than 20°. The freezing point of each alloy is marked by a prolonged period of constant temperature. The freezing points are like those of the eutectic state, and each alloy may be said to solidify at a constant temperature, as if the matter separating out had the same composition as the residual liquid. Little or no precipitate was noticed at the moment indicated by the thermometer as the commencement of freezing. Soon after 25 atoms we begin to have precipitate at the moment of freezing, and the freezing point gradually loses its resemblance to a eutectic point.

A comparison with KÜSTER's work on isomorphous mixtures strongly suggests that between 15·5 and 20 we are in the presence of one, and between 20 and 25 in presence of another, such isomorphous mixture.

At 50 atoms of tin there is a point of inflexion, and, therefore, between 60 and 70, there must be what by a stretch of language might be called a summit.

Before attempting to interpret these phenomena it will be well to consider briefly the conclusions of other workers in the same field.

RICHE ('Ann. de Ch. et Phy.,' 1873, xxx.), found that alloys of copper and tin undergo liquation, except $SnCu_4$ (20 atoms) and $SnCu_3$ (25 atoms); but he does not appear to have examined alloys between these two values.

BEHRENS, whose work, "Das Mikroscopische Gefüge der Metalle und Legierungen," is a mine of valuable information, but a mine wherein one needs to dig diligently, notes a sharp change in the colour, the microscopic structure, and the chemical behaviour of bronzes at 25 per cent., by weight, of tin. This is the same as 15·3 atomic per cents., a point where our curve shows its first angle. His microscopic study of alloys with only a few per cents. of tin shows the crystals of copper embedded in a network of white or yellowish mother substance; but at our first angle, at 15·3 atoms, all distinction in colour between crystals and mother liquor has disappeared. He says that the colour of this alloy is whitish-grey. It has a conchoidal fracture, and examined microscopically is seen to consist of bundles of parallel rods, scattered in all directions. He thinks that we have here to do with a compound $SnCu_6$. At 20 atoms of tin, our second angle, BEHRENS considers that there is another chemical compound. $SnCu_4$. He says, "that with this alloy we reach a maximum of hardness, brittleness, and resistance to chemical solvents." Also, "that if great care is taken to get an alloy of exactly this composition, we have a grey-white metal with a half-glassy, glimmering, minutely conchoidal fracture. There is no sign of crystallization; and polishing and annealing show nothing. The slower the cooling the more brittle the mass." He finds that at 25 atoms of tin the alloy is more easily attacked by reagents than at 20 atoms, and hence, and for other reasons, he refuses to accept the view that $SnCu_3$ is a compound. He is disposed to regard it as a mixture of two alloys, which may, or may not, have separated in the liquid state. He finds that this alloy crumbles under the hammer, or even under a coarse file, into polyhedra with smooth faces.

In contrast to BEHRENS, other writers have accumulated a mass of facts pointing, at least, to the unique character of the alloy with 25 atoms of tin. LAURIE finds that the electromotive force of couples formed of copper and a copper-tin alloy changes abruptly at this composition. We get here a maximum for electrical conductivity, for density, and for coefficient of dilatation.

Hence various writers have concluded that the compound $SnCu_3$ exists; but there has not been the same unanimity with regard to the existence of $SnCu_4$.

Our results, though they cannot be called final, point we think, to the view that when alloys poor in tin begin to freeze, copper separates from a liquid containing molecules of a compound of tin and copper. That when the alloy $SnCu_6$ is reached, copper ceases to separate as such; and instead, this body, or more probably an isomorphous mixture of $SnCu_6$ and $SnCu_4$, separates. The double freezing points from 18 to 20, however, show that the liquid does not solidify homogeneously, so that the isomorphism cannot be of an absolute character.

At 20 atoms of tin we think that the evidence points to the existence of the body $SnCu_4$. Between 20 and 25 atoms, perhaps the most probable explanation is to suppose that an isomorphous* mixture of $SnCu_4$ and $SnCu_3$ solidifies homogeneously. At 64 atoms of tin the curve is not incompatible with the existence of the compound $SnCu_2$, and with still more tin the molecule of any compound that may exist must ultimately, for very dilute solutions of copper in tin, contain only one atom of copper (J.C.S., *loc. cit.*).

The criticisms of BEHRENS, however, on the alloy $SnCu_3$ suggest another explanation of the phenomena which is not without probability. It may be that with more tin than $SnCu_4$, the liquid alloy breaks up into two conjugate liquids, and that this state exists until more than 25 atoms of tin are present. If this were so, we should have expected, as in the copper-lead curve, that this part would have been horizontal; but, assuming the two conjugates to differ little in density, the slight, but real, slope in this part of the curve might be accounted for by imperfect realization of equilibrium at the freezing point.

The interesting complete *cooling* curves of copper-tin alloys given by Professor ROBERTS-AUSTEN, in his Report on Alloys, will, we think, be found to be consistent with the facts observed by us, although we should not perhaps altogether agree with him in the inferences that can be drawn from these facts.

The Silver-Antimony Curve. (Fig. 11.)

In this curve it will be seen that up to 25 atomic per cents. of antimony the steepness increases with increase in the amount of antimony. As in the case of the similar feature of the tin-copper curve, we can explain this by assuming that the antimony combines with the silver to form a compound molecule.

At 25 atomic per cents. of antimony there is a well-marked angle, and although there is only one point determined between 15 and 25 atomic per cents., yet the direction of the lines leaves little doubt as to the position of this angle. The angle, therefore, corresponds to an alloy of the formula Ag_3Sb, a body that is known to exist. An angle such as we have here is not the sort of indication of the existence of a compound that the theory would lead us to expect. Indeed, another examination of this part of the curve with especially pure antimony would be needed before it would be safe to assert that the angle is at exactly Ag_3Sb.

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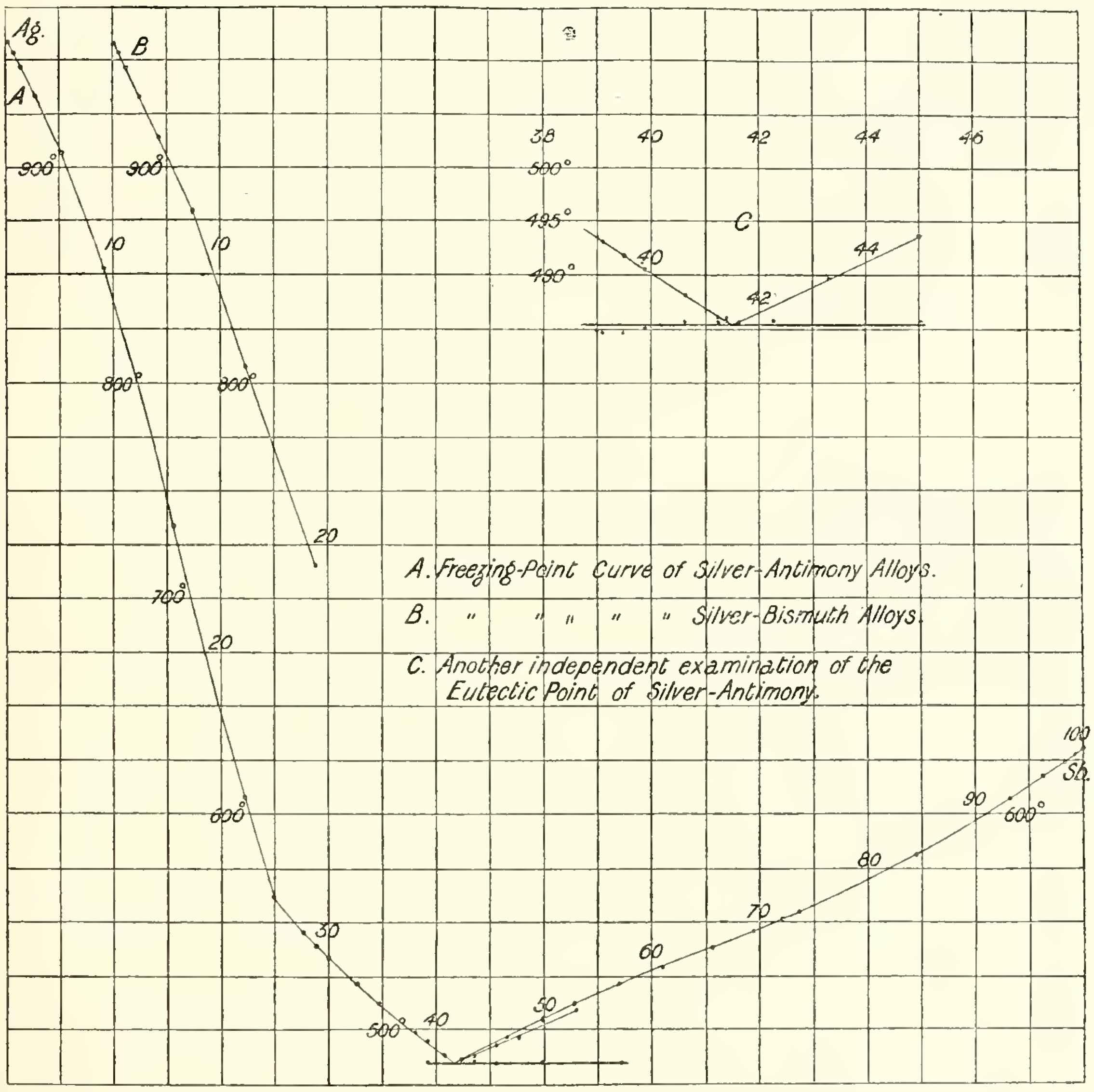
* KÜSTER, 'Zeits. Phys. Chem.,' 1890, v., p. 601.

Fig. 11.



The numbers below the curve give the Centigrade temperature.
The numbers above the curve give the atomic percentage of antimony or bismuth.

The first series, Table VIIIA., which ends at 53 atoms of antimony, involved the maintenance of the alloy at a high temperature for a good many hours, and, as the notes show, there was a considerable loss of metal. Consequently we feared that the latter part of the series might not be trustworthy. We therefore carried out a new series, Table VIIIC., beginning near the eutectic point. The result of this is given on a large scale above the main curve, and seems to show that the eutectic alloy has not a formula, although it is not very far from 40 atomic per cents. of antimony, that is, from Ag_3Sb_2. It would require the existence of a good deal of impurity in the antimony to make Ag_3Sb_2 the eutectic point.

The series, Table VIIIB., in which silver was added to antimony, gives us the same eutectic point, namely, 41·5 atomic per cents. of antimony.

The short line, starting from the eutectic point and ending at 53 atoms of antimony, was obtained with commercial antimony, so that the fact that it lies below the rest of the curve needs no comment.

The temperature 629·49° which we obtained as the freezing or melting point of antimony is almost identical with the number 629·54° that we obtained with quite different thermometers a year before ('Chem. Soc. Jour.,' 1895, p. 195). The same sample of antimony was used in both cases, and in our earlier work we noticed that this antimony behaved at its freezing point in the way peculiar to a pure substance. We think it is almost time for the text-books of chemistry to abandon the statement that antimony melts at 440°.

Incomplete Curves.

In fig. 11, the line beginning at B above the silver-antimony curve, gives the result of adding bismuth, up to 19 atomic per cents., to silver. This promises to closely resemble the silver-antimony curve, and we regret that want of time has prevented us from completing it.

In fig. 20 we give the bismuth-copper curve, which, if completed, would almost certainly resemble that of lead-copper.

Fig. 12 is the curve of gold-copper.

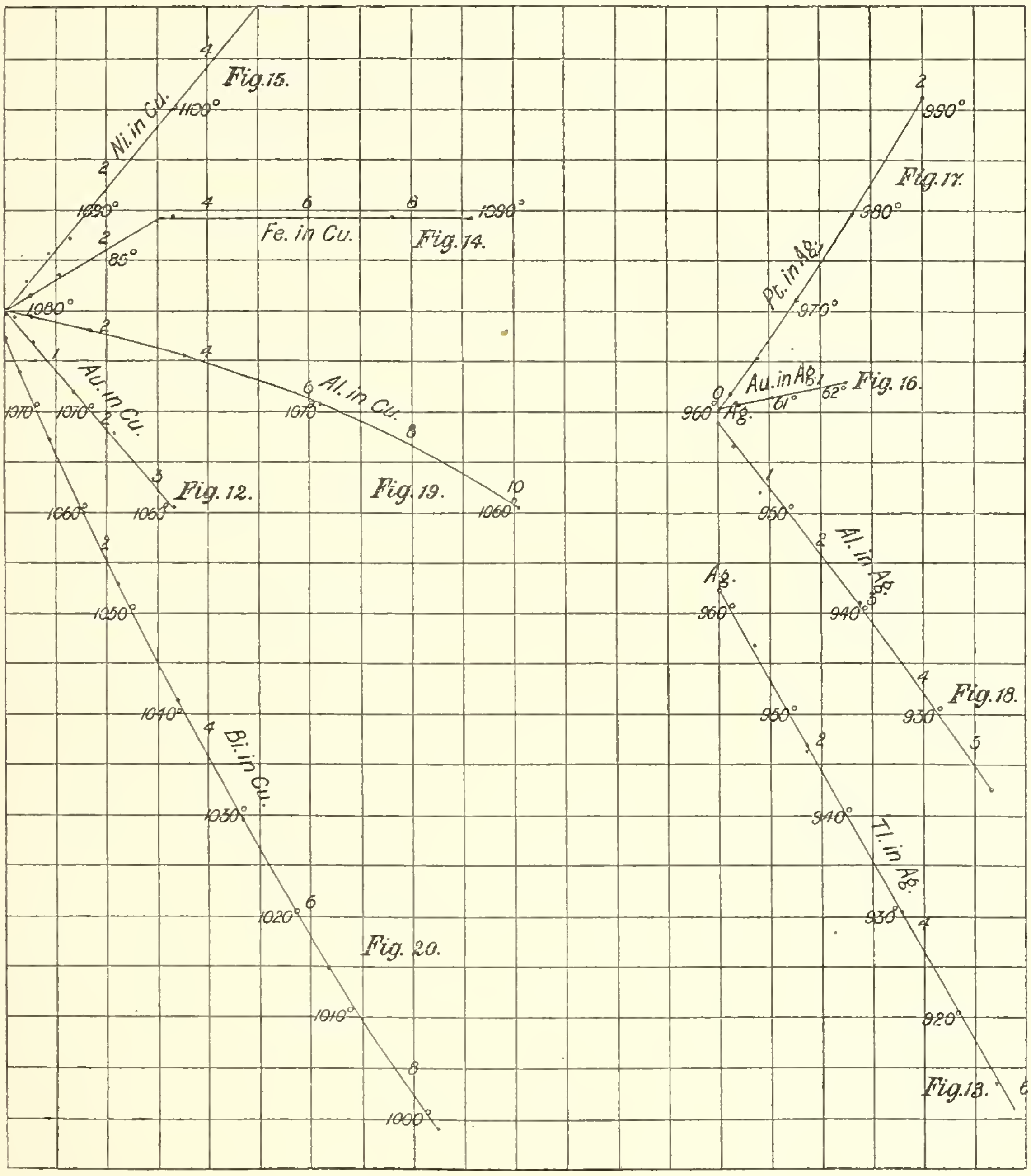
Fig. 13, the curve of thallium added to silver, is, so far as it goes, very straight, like the early part of the lead-silver curve.

The remaining metallic pairs that we have examined require further experiment, we therefore do not give tables for them; but the curves enable the numerical results to be read off with sufficient accuracy.

From figs. 14, 15, 16, 17 it will be seen that the first result of adding iron or nickel to copper, or of adding gold or platinum to silver, is to raise the freezing point. In one case only, that of iron added to copper, did we reach the higher limit of this rise; it will be seen from fig 14 that after 3 atoms of iron a further addition produces no effect on the freezing point, so that a flat occurs in the curve; we have noticed several similar cases, where zinc is the solvent metal. In these cases of rise in the freezing point we hardly think it would be profitable, until the whole curve has been traced, to attempt to distinguish between the phenomena of the separation of isomorphous mixtures, solid solutions or compounds.

In figs. 18 and 19 we give the curves for dilute solutions of aluminium in silver and in copper. We have traced these curves further, finding, as LE CHATELIER had previously found, an intermediate summit at $AlCu_3$, and probably also at $AlAg_3$; but we have been troubled by the oxidation of the aluminium, and hope to get better results. There can be little doubt that the chemical compounds formed by aluminium with other metals are unusually stable.

Figs. 12–20.



Freezing point curves for dilute solutions of metals in silver or copper.
The numbers below the curve give the Centigrade temperature.
The numbers above the curve give the atomic percentage of the dissolved metal.

The experiments described in the present paper were to a large extent carried out with apparatus purchased by funds supplied to us by the Grant Committee of the Royal Society, and we wish here to thank them for the important help that we have received in this way.

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III. *On the Relations Between the Viscosity (Internal Friction) of Liquids and their Chemical Nature.*—Part II.

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With an Appendix on the Preparation of Ethers.

By R. E. BARNETT, *B.Sc., Assoc. R.C.S.*

Received May 27,—Read June 11, 1896.

IN the Bakerian Lecture for 1894 ('Phil. Trans.,' vol. 185 A, p. 397), we gave an account of our work on the viscosity of some seventy liquids at different temperatures between 0° and the ordinary boiling-point, and we discussed the interdependence of viscosity and chemical composition. Among the liquids dealt with on that occasion, there was no member of the important series of esters or ethereal salts, and, further, only one ether—ordinary ether or ethyl oxide—was included in the list.

We therefore thought it desirable, in order to make the investigation more complete, to obtain data for members of these two classes of organic substances. The physico-chemical relationships previously established made such determinations of particular interest. Among the various connections traced between chemical constitution and viscosity, one of the most striking was the different effect which oxygen exerted upon viscosity according to the different modes in which it was assumed to be associated with other atoms in the molecule. The influence which could be ascribed to hydroxyl-oxygen differs to a most marked extent from that of carbonyl-oxygen, and, although only three cases were studied, it appeared that ether oxygen, or oxygen linked to two carbon atoms, had also a value which differed considerably from those of oxygen in other conditions. There was thus an additional reason for making observations on esters and ethers, since both contain ether-oxygen.

In what follows we give the experimental values for the ten lowest fatty esters, carefully purified samples of which had been kindly placed at our disposal by Professor SYDNEY YOUNG, F.R.S., to whom we desire to tender our thanks.

At our suggestion Mr. R. E. BARNETT, B.Sc., Assoc. R.C.S., prepared five fatty ethers, and determined their viscosity. An Appendix to this paper is devoted to an account by him of the best methods of obtaining these liquids.

As we had the opportunity of making determinations of the viscosity of three different samples of isopentane and a sample of ethyl-benzene, which had been specially prepared and purified, the values obtained are also included in this paper.

The last section of the paper deals with the discussion of the values given by the esters and ethers according to the methods adopted in our previous communication.

8.3.97

ESTERS.

Before introduction into the glischrometer each sample was distilled from a small quantity of phosphoric oxide. In every case the boiling-point was almost constant during the distillation, and agreed closely with the value found by YOUNG and THOMAS (' Chem. Soc. Trans.', vol. 63, p. 1191, 1893). For this reason it was thought unnecessary to make determinations of any other physical constants for the purpose of gauging the purity of the samples, as the densities of liquid and vapour, the critical constants, &c., have been carefully determined by YOUNG and THOMAS, and may be obtained from the paper to which reference has been made. In each case we give the boiling-point as found by us, and as given by YOUNG and THOMAS (Y. and T.). In reducing the observations on viscosity we have employed the values of the density found by YOUNG and THOMAS, and the expressions for the thermal expansion given by ELSÄSSER (' LIEBIG'S Annalen,' 218, 316).

Methyl Formate. $H.COOCH_3$.

Boiling-point constant at 31°·87. Bar., 762·6 millims. Corrected and reduced b.p. = 31°·78 (31°·8, Y. and T.).

Observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·57	100·17	·000066	·004269	0°·59	100·09	·000066	·004258
6·38	100·11	·000060	·004006	6·40	100·05	·000069	·003992
10·90	100·10	·000072	·003815	10·86	100·03	·000072	·003804
15·63	100·03	·000075	·003635	15·64	99·96	·000075	·003617
20·15	99·97	·000078	·003476	20·15	99·90	·000078	·003458
25·52	99·94	·000081	·003310	25·52	99·85	·000081	·003286
29·25	99·90	·000083	·003203	29 26	99·81	·000083	·003177

In reducing the observations we have used the value $d\,(0°/4°) = 1·00319$ for the density, and the expression

$$V = 1 + ·0_2135824\,t + ·0_410538\,t^2 - ·0_618085\,t^3$$

for the thermal expansion.

Taking

$$\eta_1 = ·004263 \quad \eta_3 = ·003190 \quad \eta_2\ (\text{calculated}) = ·003688,$$
$$t_1 = 0°·58 \quad t_3 = 29°·25 \quad t_2\ (\text{from curve}) = 13°·67,$$

we obtain the formula

$$\eta_t = \frac{0{\cdot}144673}{(68{\cdot}234 + t)^{\cdot 8325}},$$

which gives results in good agreement with the observed values.*

Ethyl Formate. $H.COOCH_2.CH_3$.

Boiling-point constant at 54°·66. Bar., 771·1 millims. Corrected and reduced b.p. = 54°·25 (54·3, Y. and T.).

Observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·45	100·19	·000053	·005028	0°·47	99·74	·000053	·005020
6·56	100·81	·000057	·004662	6·58	100·77	·000057	·004650
11·52	100·70	·000060	·004415	11·52	100·64	·000060	·004403
16·58	100·61	·000063	·004177	16·58	100·51	·000063	·004166
22·59	100·59	·000066	·003916	22·59	100·50	·000066	·003904
27·90	100·96	·000069	·003708	27·90	100·90	·000069	·003689
33·25	100·92	·000073	·003507	33·25	100·84	·000073	·003495
38·10	100·89	·000075	·003351	38·08	100·79	·000075	·003337
43·37	100·78	·000078	·003187	43·36	100·72	·000078	·003169
48·64	100·63	·000081	·003038	48·59	100·54	·000082	·003023
52·03	100·54	·000083	·002956	52·03	100·47	·000083	·002928

The value d (0°/4°) = 0·9480 for the density, and the expression

$$V = 1 + {\cdot}0_2 130917\, t + {\cdot}0_5 19198\, t^2 + {\cdot}0_7 30497\, t^3$$

for the thermal expansion, have been used in the reduction of the observations.

Taking

$$\eta_1 = {\cdot}005025 \quad \eta_3 = {\cdot}002942 \quad \eta_2 \text{ (calculated) } = {\cdot}003845,$$
$$t_1 = 0°{\cdot}46 \quad t_3 = 50°{\cdot}03 \quad t_2 \text{ (from curve) } = 24°{\cdot}22,$$

---

* To save space, it has been deemed unnecessary to give the comparisons between the observed and calculated values, as was done in the first paper. There is no longer any need to offer proof of the validity of the SLOTTE formula as an empirical expression of the relation between viscosity and temperature, especially in the case of liquids of the type now studied. It may be stated, however, that the comparison has been made in all cases, and that the general agreement is of the same order as that previously found.

we obtain the formula

$$\eta_t = \frac{22{\cdot}2406}{(139{\cdot}932 + t)^{1{\cdot}7006}},$$

which gives results in good agreement with those observed.

Propyl Formate. $H.COOCH_2.CH_2.CH_3$.

Boiling-point constant at 80°·77. Bar., 757·0 millims. Corrected and reduced b.p. = 80°·89 (80°·9, Y. and T.).

The following are the observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·35	101·51	·000040	·006646	0°·35	101·41	·000040	·006649
7·31	101·52	·000044	·006043	7·36	101·45	·000044	·006039
15·54	101·68	·000048	·005456	15·54	101·60	·000048	·005459
23·17	101·65	·000052	·004971	23·15	101·57	·000052	·004979
30·78	101·61	·000056	·004553	30·76	101·53	·000056	·004562
38·54	101·58	·000060	·004182	38·53	101·48	·000060	·004187
45·72	101·45	·000064	·003871	45·74	101·37	·000064	·003880
54·15	101·21	·000069	·003560	54·14	101·13	·000069	·003568
61·55	101·22	·000073	·003311	61·58	101·12	·000073	·003319
67·13	101·45	·000077	·003124	67·13	101·38	·000077	·003149
74·97	101·44	·000081	·002925	75·00	101·35	·000081	·002931
77·54	101·39	·000082	·002859	77·56	101·30	·000082	·002863

In reducing the observations we have used for the density at 0° the value 0·9287, and the expression

$$V = 1 + {\cdot}0_2 11903\, t + {\cdot}0_5 201033\, t^2 + {\cdot}0_7 15776\, t^3$$

for the thermal expansion.

Taking

$$\eta_1 = {\cdot}006647 \quad \eta_3 = {\cdot}002861 \quad \eta_2\,(\text{calculated}) = {\cdot}004361,$$
$$t_1 = 0^\circ{\cdot}35 \quad t_3 = 77^\circ{\cdot}55 \quad t_2\,(\text{from curve}) = 34^\circ{\cdot}72,$$

we obtain the formula

$$\eta_t = \frac{35{\cdot}3453}{(139{\cdot}283 + t)^{1{\cdot}9154}},$$

which gives values in close agreement with the observed results.

Methyl Acetate. $CH_3.COOCH_3$.

The sample boiled constantly at 57°·59. Bar., 773·6 millims. Corrected and reduced b.p. = 57°·09 (57°·1, Y. and T.).

The following are the observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·34	101·53	·000057	·004761	0°·34	101·42	·000057	·004763
6·28	101·50	·000061	·004436	6·34	101·41	·000061	·004436
11·42	101·46	·000064	·004186	11·40	101·37	·000064	·004186
16·72	101·62	·000068	·003947	16·69	101·52	·000067	·003949
22·77	101·35	·000071	·003705	22·72	101·27	·000071	·003707
28·38	101·68	·000075	·003491	28·37	101·58	·000075	·003492
33·85	101·67	·000078	·003303	33·86	101·57	·000078	·003305
40·45	101·67	·000082	·003099	40·45	101·58	·000082	·003101
46·10	101·84	·000086	·002941	46·03	101·74	·000086	·002944
50·33	101·86	·000089	·002829	50·35	101·73	·000089	·002828
54·37	101·84	·000091	·002723	54·29	101·73	·000091	·002731

The value $d\,(0°/4°) = 0·95932$, and the expression

$$V = 1 + {\cdot}0_2134982\,t + {\cdot}0_687098\,t^2 + {\cdot}0_735562\,t^3,$$

have been used in the reduction of the observations.

Taking

$$\eta_1 = {\cdot}004762 \quad \eta_3 = {\cdot}002727 \quad \eta_2\,(\text{calculated}) = {\cdot}003604,$$
$$t_1 = 0°{\cdot}34 \quad t_3 = 54°{\cdot}33 \quad t_2\,(\text{from curve}) = 25°{\cdot}32,$$

we obtain the formula

$$\eta_t = \frac{57{\cdot}4012}{(154{\cdot}499 + t)^{1{\cdot}8636}},$$

which gives results almost identical with those observed.

Ethyl Acetate. $CH_3.COOCH_2.CH_3$.

The boiling-point was constant at 77°·25. Bar. 761·8 millims. Corrected and reduced b.p. = 77°·18 (77°·15, Y. and T.).

The results of the viscosity observations are as follows :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·24	100·50	·000045	·005767	0°·26	100·42	·000045	·005759
8·90	100·47	·000050	·005146	8·89	100·38	·000050	·005142
14·50	100·07	·000053	·004789	14·43	100·10	·000053	·004802
21·38	100·24	·000057	·004413	21·37	100·25	·000057	·004424
28·14	99·86	·000061	·004093	28·11	99·83	·000061	·004099
36·58	100·11	·000066	·003734	36·50	100·08	·000066	·003742
44·12	99·81	·000070	·003452	44·12	99·77	·000070	·003459
51·18	100·39	·000075	·003224	51·12	100·30	·000075	·003224
60·18	100·38	·000080	·002960	60·15	100·32	·000080	·002960
68·50	100·41	·000085	·002737	68·37	100·33	·000085	·002746
74·61	100·50	·000089	·002593	74·58	100·42	·000089	·002595

In reducing the observations we have used $d\ (0^\circ/4^\circ) = 0{\cdot}92436$, and the expresssion

$$V = 1 + {\cdot}0_2 12185\, t + {\cdot}0_5 45587\, t^2 - {\cdot}0_8 76926\, t^3.$$

Taking

$$\eta_1 = {\cdot}005763 \qquad \eta_3 = {\cdot}002594 \qquad \eta_2\,(\text{calculated}) = {\cdot}003866,$$
$$t_1 = 0^\circ{\cdot}25 \qquad t_3 = 74^\circ{\cdot}60 \qquad t_2\,(\text{from curve}) = 33^\circ{\cdot}38,$$

we obtain the formula

$$\eta_t = \frac{45{\cdot}322}{(135{\cdot}423 + t)^{1{\cdot}8268}},$$

which satisfactorily reproduces the observed values.

Propyl Acetate. $CH_3.COOCH_2.CH_2.CH_3$.

The sample boiled between 101°·93 and 102°·00. Bar., 770·6 millims. Corrected and reduced b.p. = 101°·52 (101°·55, Y. and T.).

Observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·39	101·04	·000034	·007649	0°·38	101·03	·000034	·007674
9·78	100·95	·000039	·006645	9·79	100·87	·000039	·006673
20·59	100·81	·000044	·005757	20·59	100·79	·000044	·005768
30·15	100·86	·000049	·005102	30·11	100·81	·000049	·005115
39·76	100·93	·000054	·004562	39·75	100·86	·000054	·004564
50·37	100·98	·000060	·004064	49·71	100·89	·000059	·004097
61·37	101·00	·000066	·003621	61·35	100·93	·000066	·003628
69·90	101·01	·000071	·003328	69·89	100·92	·000071	·003334
80·03	100·97	·000076	·003027	79·98	100·90	·000076	·003030
89·50	100·99	·000082	·002775	89·50	100·90	·000082	·002775
96·97	100·99	·000086	·002604	96·84	100·91	·000086	·002600

The value 0·91016 for the density at 0°, and the expression

$$V = 1 + {\cdot}0_2 119136\, t + {\cdot}0_6 41636\, t^2 + {\cdot}0_7 195991\, t^3,$$

have been used in reducing the observations.

Taking

$$\eta_1 = {\cdot}007661 \quad \eta_3 = {\cdot}002602 \quad \eta_2 \text{ (calculated)} = {\cdot}004465,$$
$$t_1 = 0^\circ{\cdot}39 \quad t_3 = 96^\circ{\cdot}75 \quad t_2 \text{ (from curve)} = 41^\circ{\cdot}76,$$

we obtain the formula

$$\eta_t = \frac{73{\cdot}6005}{(125{\cdot}269 + t)^{1{\cdot}8972}},$$

which gives values in good agreement with those of observation.

Methyl Propionate. $CH_3.CH_2.COOCH_3$.

The boiling-point was constant at 79°·66. Bar., 759·1 millims. Corrected and reduced b.p. = 79°·70 (79°·67, Y. and T.).

Observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·39	100·34	·000046	·005789	0°·37	100·25	·000046	·005787
9·73	100·33	·000051	·005139	9·73	100·25	·000051	·005145
16·81	100·26	·000055	·004719	16·77	100·22	·000055	·004731
23·70	100·27	·000059	·004363	23·21	100·21	·000059	·004372
29·61	100·23	·000062	·004096	29·62	100·13	·000062	·004100
38·67	100·23	·000067	·003746	38·65	100·14	·000067	·003746
45·58	100·22	·000071	·003472	45·60	100·12	·000071	·003481
52·64	100·54	·000075	·003253	52·67	99·82	·000075	·003256
60·38	100·39	·000080	·003027	60·37	100·33	·000080	·003029
68·55	100·39	·000085	·002807	68·43	100·30	·000084	·002816
75·86	100·40	·000089	·002638	73·84	100·31	·000089	·002636

We have used 0·9387 as the value of the density at 0°, and the expression

$$V = 1 + {\cdot}0_2 13049\, t + {\cdot}0_5 13275\, t^2 + {\cdot}0_7 46943\, t^3$$

in reducing the observations.

Taking

$$\eta_1 = {\cdot}005788 \quad \eta_3 = {\cdot}002677 \quad \eta_2 \text{ (calculated)} = {\cdot}003907,$$

$$t_1 = 0^\circ{\cdot}38 \quad t_3 = 75^\circ{\cdot}85 \quad t_2 \text{ (from curve)} = 34^\circ{\cdot}22,$$

we obtain the formula

$$\eta_t = \frac{74{\cdot}898}{(146{\cdot}621 + t)^{1{\cdot}89725}},$$

which gives values which agree closely with those observed.

Ethyl Propionate. $CH_3.CH_2.COOCH_2 . CH_3.$

The boiling-point varied between 98°·95 and 99°·03. Bar., 756·5 millims. Corrected and reduced b.p. = 99°·14 (99°·0, Y. and T.).

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
° 0·43	100·71	·000038	·006884	° 0·35	100·69	·000037	·006896
10·12	100·15	·000042	·006032	10·06	100·20	·000042	·006042
20·10	99·53	·000047	·005310	20·07	99·60	·000047	·006323
29·74	98·97	·000052	·004733	29·73	98·96	·000051	·004738
39·88	98·85	000057	·004226	39·87	98·81	·000057	·004235
49·64	98·69	·000062	·003818	49·72	98·70	·000062	·003817
59·12	99·91	·000068	·003477	59·16	99·82	·000068	·003478
69·23	99·87	·000074	·003148	69·24	99·78	·000074	·003162
72·12	99·55	·000075	·003072	72·12	99·50	·000075	·003075
80·04	99·50	·000079	·002855	80·25	99·45	·000079	·002854
89·68	99·50	·000085	·002627	89·70	99·42	·000085	·002627

In reducing the observations we have used 0·91240 for the density at 0°, and the expression

$$V = 1 + {\cdot}0_2119971\,t + {\cdot}0_514867\,t^2 + {\cdot}0_710599\,t^3$$

for the thermal expansion.

Taking

$$\eta_1 = {\cdot}006890 \quad \eta_3 = {\cdot}004254 \quad \eta_2 \text{ (calculated)} = {\cdot}004254,$$

$$t_1 = {\cdot}0^\circ{\cdot}39 \quad t_3 = 89^\circ{\cdot}69 \quad t_2 \text{ (from curve)} = 39^\circ{\cdot}38,$$

we obtain the formula

$$\eta_t = \frac{72{\cdot}981}{(133{\cdot}905 + t)^{1{\cdot}8914}},$$

which gives values in close concordance with those of observation.

Methyl Butyrate. $CH_3.CH_2.CH_2.COOCH_3$.

The sample distilled between 102°·65 and 102°·67. Bar., 758·8 millims. Corrected and reduced b.p. = 102°·67 (102°·75, Y. and T.).

Observations on viscosity gave the following results :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·38	101·34	·000035	·007544	0°·26	101·32	·000035	·007558
10·49	101·22	·000040	·006524	10·41	101·16	·000040	·006531
20·37	101·04	·000045	·005729	20·39	100·99	·000045	·005726
30·68	100·85	·000050	·005048	30·59	100·82	·000050	·005051
40·62	100·56	·000055	·004499	40·54	100·51	·000055	·004507
50·25	100·16	·000060	·004058	50·35	100·21	·000060	·004058
60·19	100·14	·000065	·003667	60·22	100·05	·000065	·003668
71·59	100·34	·000071	·003288	71·40	100·26	·000071	·003302
79·56	100·31	·000076	·003053	79·35	100·24	·000076	·003061
90·64	100·39	·000082	·002765	90·62	100 29	·000082	·002770
98·14	100 42	·000086	·002593	98·42	100·47	·000086	·002591

In reducing the observations, we have used $d\,(0°/4°) = 0{\cdot}92006$ for the density, and the expression

$$V = 1 + {\cdot}0_2113062\,t + {\cdot}0_524809\,t^2 + {\cdot}0_836230\,t^3$$

for the thermal expansion.

Taking

$$\eta_1 = {\cdot}007551 \qquad \eta_3 = {\cdot}002597 \qquad \eta_2\ (\text{calculated}) = {\cdot}004428,$$
$$t_1 = 0°{\cdot}32 \qquad t_3 = 98°{\cdot}03 \qquad t_2\ (\text{from curve}) = 42°{\cdot}13,$$

the formula

$$\eta_t = \frac{53{\cdot}0991}{(123{\cdot}745 + t)^{1{\cdot}8375}}$$

is obtained, which satisfactorily reproduces the observed values.

Methyl Isobutyrate. $(CH_3)_2.CH.COOCH_3$.

The sample boiled between 92°·03 and 92°·05. Bar., 754·8 millims. Corrected and reduced b.p. = 92°·26 (92°·3, Y. and T.).

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
° 0·35	100·06	·000039	·006682	° 0·22	100·08	·000039	·006696
9·48	99·97	·000043	·005904	9·32	99·89	·000043	·005925
18·12	99·91	·000047	·005297	18·11	99·82	·000047	·005301
28·99	101·36	·000054	·004660	28·97	101·26	·000054	·004660
35·82	101·16	·000057	·004314	35·80	101·19	·000057	·004320
44·70	100·99	·000062	·003928	44·63	101·04	·000062	·003937
52·56	100·91	·000066	·003626	52·54	100·84	·000066	·003636
62·64	101·23	·000072	·003289	62·81	100·74	·000072	·003289
76·20	101·25	·000077	·003035	76·24	101·18	·000077	·003038
79·78	101·19	·000082	·002814	79·76	101·11	·000082	·002812
88·83	101·22	·000087	·002587	88·86	101·13	·000087	·002590

The value 0·91131 for the density at 0°, and the expression

$$V = 1 + \cdot0_{2}12170\,t + \cdot0_{6}38334\,t^{2} + \cdot0_{7}22582\,t^{3}$$

have been used in reducing the observations.

Taking

$$\eta_1 = \cdot006689 \quad \eta_3 = \cdot002589 \quad \eta_2\ (\text{calculated}) = \cdot004161,$$
$$t_1 = 0^\circ\cdot33 \quad t_3 = 88^\circ\cdot84 \quad t_2\ (\text{from curve}) = 39^\circ\cdot20,$$

we obtain the formula

$$\eta_t = \frac{98\cdot0935}{(139\cdot956 + t)^{1\cdot9405}},$$

which gives values agreeing fairly well with the observed numbers.

ETHERS.

Methyl Propyl Ether. $CH_3.O.CH_2.CH_2.CH_3$.

A sample prepared from methyl iodide and sodium propylate was distilled from sodium wire, and the portion boiling between 39°·20 and 39°·28 was used in the observations. Bar., 762·5 millims. Corrected and reduced b.p. = 39°·15.

The following are the observations of viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·30	101·83	·000069	·003064	0°·30	101·78	·000069	·003065
5·16	101·65	·000072	·002912	5·12	101·62	·000072	·002916
10·47	102·60	·000076	·002757	10·47	102·53	·000076	·002761
15·17	102·53	·000079	·002630	15·18	102·48	·000079	·002630
20·09	102·49	·000082	·002514	20·11	102·42	·000082	·002512
25·74	102·48	·000085	·002385	25·72	102·41	·000085	·002385
29·43	102·00	·000087	·002300	29·53	102·08	·000087	·002301
35·03	101·61	·000090	·002187	35·28	101·65	·000090	·002187

In reducing the observations, Zander's value, 0·7420 for the density at 0°, and his expression

$$V = 1 + \cdot0_{2}14406\,t + \cdot0_{6}99286\,t^2 + \cdot0_{7}58817\,t^3$$

for the thermal expansion ('Annalen,' 243, 2), have been employed.

Taking

$$\eta_1 = \cdot003064 \quad \eta_3 = \cdot002187 \quad \eta_2\ (\text{calculated}) = \cdot002589,$$
$$t_1 = 0^\circ\cdot30 \qquad t_3 = 35^\circ\cdot15 \qquad t_2\ (\text{from curve}) = 16^\circ\cdot80,$$

the formula

$$\eta_t = \frac{8\cdot4251}{(146\cdot862 + t)^{1\cdot5863}}$$

is obtained, which satisfactorily reproduces the observed values.

Ethyl Propyl Ether. $CH_3.CH_2.O.CH_2.CH_2.CH_3$.

Prepared from ethyl iodide and sodium propylate and dried over sodium wire. The portions used for viscosity observations boiled from 62°·93 to 62°·98. Bar., 747·7 millims. Corrected and reduced b.p. = 63°·44.

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·32	101·38	·000054	·003955	0°·38	101·31	·000054	·003950
5·66	101·30	·000057	·003709	5·64	101·22	·000057	·003719
10·63	101·23	·000060	·003511	10·68	101·15	·000060	·003510
15·65	101·14	·000063	·003323	15·67	101·10	·000063	·003326
20·38	101·10	·000065	·003162	20·27	101·04	·000065	·003169
25·39	102·01	·000069	·003005	25·30	101·96	·000070	·003006
30·11	102·00	·000072	·002863	30·06	101·92	·000072	·002864
35·12	101·91	·000074	·002725	35·04	101·89	·000074	·002729
39·96	101·75	·000077	·002600	40·01	101·69	·000077	·002597
45·63	101·59	·000080	·002466	45·62	101·52	·000080	·002466
50·35	101·53	·000083	·002364	50·25	101·49	·000083	·002362
55·06	101·40	·000086	·002262	54·95	101·36	·000086	·002266
60·32	101·32	·000089	·002157	60·03	101·32	·000089	·002161

The value 0·7544 for the density at 0°, and the expression

$$V = 1 + {\cdot}0_2 13116\, t + {\cdot}0_5 26162\, t^2 + {\cdot}0_7 15617\, t^3,$$

given by Dobriner ('Annalen,' 243, 4), have been employed in reducing the observations.

Taking

$$\eta_1 = {\cdot}003953 \quad \eta_3 = {\cdot}002159 \quad \eta_2\,(\text{calculated}) = {\cdot}002921,$$
$$t_1 = 0^\circ{\cdot}35 \quad t_3 = 60^\circ{\cdot}18 \quad t_2\,(\text{from curve}) = 28^\circ{\cdot}16,$$

the formula

$$\eta_t = \frac{284{\cdot}675}{(183{\cdot}355 + t)^{2{\cdot}1454}}$$

is obtained. The agreement between the observed and calculated values is remarkably close.

Dipropyl Ether. $CH_3.CH_2.CH_2.O.CH_2.CH_2.CH_3$.

Prepared by Krafft's method, and submitted to repeated fractionation from sodium wire. The fraction used in the determinations of viscosity boiled between 89°·86 and 89°·90. Bar. 760·8 millims. Corrected and reduced b.p. = 89°·84.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
° 0·53	101·92	·000041	·005359	° 0·64	101·91	·000041	·005359
8·62	101·76	·000045	·004821	8·53	101·77	·000045	·004831
16·96	101·35	·000049	·004355	16·94	101·30	·000049	·004362
24·66	101·29	·000053	·003980	24·65	101·26	·000053	·003990
32·44	101·12	·000057	·003653	32·47	101·06	·000059	·003656
40·46	102·27	·000062	·003359	40·48	102·31	·000062	·003361
48·03	101·93	·000065	·003113	48·10	101·86	·000065	·003115
56·15	101·86	·000070	·002877	56·14	101·82	·000070	·002876
64·18	101·71	·000074	·002662	64·14	101·69	·000074	·002667
72·48	101·35	·000078	·002468	72·70	101·32	·000078	·002470
81·53	101·23	·000083	·002280	81·42	101·19	·000083	·002288
88·00	101·25	·000087	·002154	88·03	101·17	·000087	·002154

The value d (0°/0°) = 0·7633 for the relative density, and the expression

$$V = 1 + {\cdot}0_2 12132\, t + {\cdot}0_5 39318\, t^2 - {\cdot}0_7 13644\, t^3,$$

obtained by Zander ('Annalen,' 214, 163), have been used in reducing the observations.

Taking

$$\eta_1 = \cdot005359 \quad \eta_3 = \cdot002154 \quad \eta_2\,(\text{calculated}) = \cdot003398,$$
$$t_1 = 0^\circ\cdot58 \quad t_3 = 88^\circ\cdot01 \quad t_2\,(\text{from curve}) = 39^\circ\cdot27,$$

the formula

$$\eta_t = \frac{104\cdot068}{(148\cdot362 + t)^{1\cdot9734}}$$

is obtained, which gives values in good agreement with those observed.

Methyl Isobutyl Ether. $CH_3.O.CH_2.CH.(CH_3)_2$.

Prepared from methyl iodide and sodium isobutylate and fractionated from sodium wire. In the case of this ether the process appeared to work more satisfactorily than in any of the others, the yield being almost quantitative. Two series of viscosity observations were made on this substance.

The fraction used in the first set boiled between 59°·40 and 59°·43; bar. 763·8 millims.; corrected and reduced b.p. = 59°·26. After the viscosity observations had been completed, this fraction was digested for two days with phosphoric oxide, and again distilled.

The corrected and reduced boiling-point was practically the same as before, viz., 59°·29. A second set of viscosity observations was then made with this liquid, and as the results were practically identical with those of the first set, the second only are given below. A combustion gave the following results;—

	Found.	Calculated.
Carbon	68·22	68·18
Hydrogen.	13·64 . .	13·64

Observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·37	102·83	·000057	·003797	0°·36	102·78	·000057	·003797
7·00	102·76	·000061	·003524	6·85	102·75	·600061	·003528
14·54	102·66	·000065	·003247	14·48	102·61	·000065	·003245
21·31	102·65	·000069	·003021	21·40	102·58	·000069	·003023
28·92	102·47	·000073	·002796	28·86	102·42	·000973	·002804
35·98	102·31	·000077	·002619	35·98	102·28	·000077	·002620
42·50	102·26	·000081	·002461	42·60	102·19	·000081	·002455
49·64	102·22	·000085	·002309	49·86	102·15	·000085	·002302
55·24	102·10	·000088	·002193	55·21	102·06	·000088	·002192

As the thermal expansion of methyl isobutyl ether had not previously been determined, a series of measurements had to be made with the dilatometer, in order to obtain the data required for the reduction of the observations on viscosity. The apparatus and method employed were those described by THORPE ('Chem. Soc. Trans.,' vol. 63, p. 262, 1893).

The observations with the dilatometer gave :—

T.	Obs.	Calc.	T.	Obs.	Calc.
0·0	2126·98	2126·76	30·83	2219·52	2219·41
4·82	2140·45	2140·48	35·01	2232·90	2232·94
10·71	2157·43	2157·62	40·48	2250·96	2251·03
16·76	2175·55	2175·64	46·06	2269·89	2269·97
20·75	2187·78	2187·79	49·33	2281·33	2281·29
25·80	2203·56	2203·46	54·23	2298·63	2298·59

The observed values lead to the following formula :—

$$V = 2126{\cdot}76 + 2{\cdot}8216833\, t + {\cdot}00536623\, t^2 + {\cdot}00001901\, t^3,$$

from which the calculated values are obtained.

Dividing by the first term and correcting for the expansion of glass, the formula for the absolute expansion is found to be

$$V_t = 1 + {\cdot}0_2135624\, t + {\cdot}0_5256232\, t^2 + {\cdot}0_890132\, t^3.$$

From this is calculated the following table giving the volumes of methyl isobutyl ether for every 10° between 0° and its boiling-point :—

T.	Vol.	Diff.	T.	Vol.	Diff.
0	100000		30	104324	759
5	100685	685	35	105099	775
10	101383	698	40	105893	794
15	102095	712	45	106704	811
20	102822	727	50	107534	830
25	103565	743	55	108384	850

The density at 0° was found to be 0·7507.

Taking

$$\eta_1 = {\cdot}003797 \quad \eta_3 = {\cdot}002192 \quad \eta_2\ (\text{calculated}) = {\cdot}002885,$$
$$t_1 = 0^\circ{\cdot}36 \quad t_3 = 55^\circ{\cdot}22 \quad t_2\ (\text{from curve}) = 25^\circ{\cdot}92,$$

the formula

$$\eta_t = \frac{122·591}{(174·318 + t)^{2·0109}}$$

is obtained, which gives values agreeing well with those observed.

Ethyl Isobutyl Ether. $CH_3.CH_2O.CH_2CH.(CH_3)_2$.

A sample prepared from ethyl iodide and sodium isobutylate was distilled from sodium wire, and the portion boiling between 80°·74 and 80°·79 was collected separately. Bar. 750·2 milims. Corrected and reduced b.p. = 81°·18.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp. °	Press.	Corr.	η.	Temp. °	Press.	Corr.	η.
0·36	103·68	·000046	·004800	0·36	103·69	·000046	·004807
7·34	103·26	·000049	·004396	7·34	103·29	·000049	·004399
15·13	101·98	·000053	·004001	15·07	101·96	·000053	·004006
21·61	101·58	·000056	·003708	21·80	101·58	·000056	·003711
28·22	101·58	·000060	·003449	28·06	101·31	·000060	·003458
35·41	101·39	·000064	·003200	35·38	101·36	·000064	·003200
41·80	100·87	·000067	·002992	41·72	100·82	·000067	·003000
48·94	104·00	·000073	·002793	49·00	103·97	·000073	·002790
56·97	102·39	·000076	·002613	56·01	102·34	·000076	·002617
63·18	102·25	·000080	·002439	63·16	102·11	·000080	·002441
70·69	102·16	·000084	·002277	70·64	102·11	·000084	·002282
77·43	102·04	·000088	·002147	77·53	102·01	·000088	·002148

As in the case of methyl isobutyl ether, determinations had to be made of the thermal expansion of this liquid.

The observations with the dilatometer gave :—

T.	Obs.	Calc.	T.	Obs.	Calc.
0·0	2126·13	2125·89	48·09	2267·85	2267·87
6·51	2143·50	2143·65	56·31	2295·19	2295·15
16·33	2171·10	2171·20	63·84	2320·91	2321·06
23·87	2193·00	2193·03	71·97	2350·27	2350·12
32·02	2217·41	2217·37	76·50	2366·82	2366·83
40·17	2242·52	2242·54			

The observed values lead to the formula :—

$$V = 2125·89 + 2·7009474\, t + ·00416124\, t^2 + ·00002225\, t^3,$$

from which the calculated values are obtained.

Dividing by the first term, and correcting for the expansion of glass, the formula for the absolute expansion is found to be

$$V = 1 + \cdot0_2129999\,t + \cdot0_5199488\,t^2 + \cdot0_7105254\,t^3.$$

From this is calculated the following table, giving the volumes of ethyl isobutyl ether for every 5° between 0° and its boiling-point :—

T.	Vol.	Diff.	T.	Vol.	Diff.
0	100000		45	106350	763
5	100655	655	50	107130	783
10	101321	666	55	107929	799
15	101998	677	60	108745	816
20	102688	690	65	109582	837
25	103391	703	70	110438	856
30	104108	717	75	111316	878
35	104839	731	80	112216	900
40	105587	748			

A determination of the density at 0° gave 0·75445. This value and the above expression for the thermal expansion were used in reducing the observations for viscosity.

Taking

$$\eta_1 = \cdot004804 \quad \eta_3 = \cdot002147 \quad \eta_2\ (\text{calculated}) = \cdot003212,$$
$$t_1 = 0^\circ{\cdot}36 \quad t_3 = 77^\circ{\cdot}48 \quad t_2\ (\text{from curve}) = 35^\circ{\cdot}00,$$

the formula

$$\eta_t = \frac{98{\cdot}4046}{(152{\cdot}69 + t)^{1{\cdot}9733}}$$

is obtained, which gives values agreeing satisfactorily with the observed numbers.

Isopentane. $(CH_3).CH.CH_2.CH_3$.

In our previous communication we gave a series of values of the viscosity coefficients of a sample of isopentane lent to us by the late Professor SCHORLEMMER. The quantity of liquid was very small, and the boiling-point varied by nearly 3° during the distillation. For these reasons, and also from the fact that the sample was obtained from petroleum, we thought it advisable to make additional observations on the viscosity of this substance, and, if possible, on a product obtained from a different source.

We have been able to examine three different samples of isopentane made respectively from English, Scotch, and Irish fusel oil by direction of the Photometric

Standards Committee, in the laboratory of the Royal College of Science, by Mr. ALFRED GREEVES.

The English fusel oil was obtained from potato spirit, the Scotch from spirit prepared from a mixture of maize and barley, and the Irish from spirit made from barley alone. In each case the fusel oil was fractionated, and the portion boiling between 128° and 132° was used in the preparation of the isopentane.

The alcohol was converted into the iodide, which was washed with a solution of soda, then with water, and after drying over calcium chloride was carefully fractionated.

The iodide was reduced by means of a copper-zinc couple, and the mixture of isopentane and amylene thus produced was placed over excess of bromine for two days. The product was then separated from the bromine, washed with an ice-cold solution of soda, and then submitted to fractionation, which affords a ready method of separating the isopentane from amylene dibromide. As a further precaution against the presence of traces of amylene, amylene dibromide, or amyl iodide, the product was treated with fuming sulphuric acid for some hours. As this acid attacks isopentane to some extent, on removal from the acid the product was washed with dilute soda and then with water to remove sulphur dioxide; it was next dried over ordinary sulphuric acid for some days, then over sodium wire, and finally submitted to fractionation.

The observed boiling-points were :—

I.	From English amyl alcohol . .	28°·17 to 28°·27.	Bar., 765·9 millims.
II.	,, Scotch ,, ,, . .	28°·10 to 28°·12.	,, 762·5 ,,
III.	,, Irish ,, ,, . .	27°·65 to 27°·70.	,, 750·3 ,,

Corrected and reduced boiling-points :—

I.	II.	III.
27°·99	28°·04	28°·04

These values are considerably lower than most of the published determinations of the boiling-point of isopentane. They are almost identical, however, with that recently found by YOUNG, and by YOUNG and THOMAS, viz., 27°·95 ('Proc. Phys. Soc.,' vol. 13, pp. 607 and 666, 1895).

Determinations of vapour density :—

	I.	II.	III.	
Found	36·05	35·78	35·55	
	35·61	35·62	35·63	Calculated, 35·83.

The following are the observations for viscosity :—

I.

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0·45°	99·68	·000064	·002785	0·44°	99·61	·000064	·002782
5·16	99·60	·000066	·002651	5·15	99·55	·000066	·002644
10·82	99·57	·000069	·002514	10·85	99·50	·000069	·002491
15·33	99·53	·000072	·002393	15·34	99·48	·000072	·002383
20·29	99·51	·000074	·002282	20·22	99·47	·000075	·002275
25·16	99·53	·000077	·002174	25·15	99·48	·000077	·002170

II.

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0·35°	100·05	·000064	·002759	0·37°	100·03	·000064	·002760
5·68	99·95	·000067	002607	5·67	99·93	·000067	·002606
10·21	99·84	·000070	·002488	10·04	99·80	·000070	·002494
15·67	100·58	·000074	·002354	15·65	100·56	·000074	·002357
20·46	100·55	·000076	·002244	20·46	100·50	·000076	·002248
23·90	100·53	·000078	·002172	23·88	100·46	·000078	·002171

III.

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0·31°	101·18	·000065	·002767	0·35°	101·14	·000065	·002765
5·62	101·11	·000068	·002612	5·60	101·05	·000068	·002607
10·90	101·03	·000071	·002471	10·94	100·97	·000071	·002472
16·02	100·84	·000074	·002357	15·97	100·83	·000073	·002361
19·87	100·73	·000076	·002262	19·88	100·69	·000076	·002268
23·44	100·68	·000078	·002185	23·49	100·64	·000078	·002193

In reducing the observations we have used Professor YOUNG's value, 0·6392 for the density at 0°, and the expression

$$V = 1 + \cdot 0_2 146834\, t + \cdot 0_5 509626\, t^2 + \cdot 0_8 6979\, t^3,$$

given by THORPE and JONES (*loc. cit.*).

The comparison of the values given by these three samples with those given by the petroleum sample (A.) is contained in the following table.

In the case of each sample two curves were plotted, and the coefficients were read off at every 5°. The means of these values are given in the table, which also shows at each temperature-interval the differences between the coefficients of samples II., III., and A, and that of I.

Temp.	I.	II.		III.		A.	
	η.	η.	Difference.	η.	Difference.	η.	Difference.
0°	·002797	·002769	·000028	·002776	·000021	·002726	·000071
5	·002651	·002624	·000027	·002627	·000024	·002583	·000068
10	·002521	·002494	·000027	·002495	·000026	·002456	·000065
15	·002398	·002371	·000027	·002375	·000023	·002340	·000058
20	·002283	·002255	·000028	·002264	·000019	·002233	·000050
25	·002175	·002149	·000026	·002158	·000017	·002130	·000045

The table shows that no two samples gave precisely the same values, No. I.—the isopentane derived from potato spirit, giving the largest, and A—the isopentane from petroleum, the smallest value.

The values given by No. I. are about 1·1 per cent. larger than those given by No. II., and 0·9 per cent. larger than those given by No. III., whilst they are 2·5 per cent. larger than those given by the petroleum hydrocarbon. It is evident, therefore, that the isopentane from petroleum was not a pure product, and further that on preparing the hydrocarbon from amyl alcohol in the manner just described, although the boiling-points and vapour-densities of the three samples are practically the same, yet, as regards their viscosities, slight differences can be detected, which can only be due to the difference in the origin of the samples.

Apparently, the lower the boiling-point and the higher the viscosity the more likely is it that the substance is pure; we, therefore, regard the values for η given by No. I. as nearest to the truth. It may be that isoamylene, which is less viscous than isopentane, may be present to some extent in Nos. II. and III.

In what follows we have used the coefficients given by No. I. sample.

Taking

$$\eta_1 = \cdot002783 \quad \eta_3 = \cdot002172 \quad \eta_2\,(\text{calculated}) = \cdot002458,$$
$$t_1 = 0^\circ\cdot44 \quad t_3 = 25\cdot15 \quad t_2\,(\text{from curve}) = 12^\circ\cdot50,$$

we obtain the formula

$$\eta_t = \frac{391\cdot101}{(208\cdot6 + t)^{2\cdot2186}};$$

which gives numbers in close agreement with those observed.

Mean. temp.	η.		Difference.
	Observed (mean).	Calculated.	
0°·44	·002783	·002783	000000
5·15	·002647	·002649	−·000002
10·83	·002502	·002499	+·000003
15·33	·002388	·002389	−·000001
20·25	·002279	·002276	+·000003
25·15	·002172	·002172	000000

The above coefficients are, on the average, only about 1·5 per cent. smaller than those found for normal pentane, whereas the numbers given by the original sample of isopentane were about 4 per cent. smaller.

On substituting the above for the original values, the relationships previously traced between the viscosity magnitudes of the paraffins are slightly altered. Since, however, all the lower paraffins we examined were prepared from petroleum, we do not at present propose to make the substitution, as the values already given probably express the relative effect of chemical nature more correctly than would be the case if the hydrocarbons were prepared partly by other methods. As regards the absolute value of the viscosity coefficients, there can be little doubt that the numbers afforded by the isopentane from amyl alcohol are to be preferred.

Ethyl Benzene. $C_6H_5.CH_2.CH_3$.

The specimen of ethyl benzene previously examined was prepared by fractionating a sample obtained from KAHLBAUM, whereas its three isomers, the xylenes, were prepared for us by Dr. G. T. MOODY from the pure sodium salts of the corresponding sulphonic acids. As Dr. MOODY kindly placed at our disposal a quantity of ethyl benzene, also prepared from the sodium salt of its sulphonic acid, a substance crystallizing in beautiful plates and having the formula $C_6H_4.C_2H_5.SO_3Na + \frac{1}{2}H_2O$, we carried out a fresh series of viscosity observations.

On distilling from sodium wire, the boiling-point varied between 136°·05 and 136°·10. Bar., 764·3 millims. Corrected and reduced b.p. 135°·86.

The value given by the original sample was 135°·92.

The following are the viscosity observations :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·28	100·74	·000029	·008699	0°·27	100·65	·000029	·008706
14·35	100·68	·000035	·007149	14·22	100·62	·000035	·007166
24·98	100·69	·000039	·006252	25·02	100·63	·000039	·006258
39·86	100·75	·000046	·005270	39·84	100·67	·000046	·005281
53·60	100·73	·000052	·004573	53·38	100·65	·000052	·004580
65·42	101·10	·000058	·004076	65·39	101·04	·000058	·004080
77·68	101·14	·000063	·003650	77·66	101·06	·000063	·003654
89·84	101·15	·000069	·003296	89·86	101·06	·000069	·003291
105·96	100·48	·000076	·002900	105·93	100·39	·000076	·002901
119·16	100·53	·000082	·002622	119·17	100·46	·000082	·002625
131·89	100·57	·000088	·002392	131·97	100·49	·000088	·002390

In reducing the observations we have used the value 0·8832 for the density at 0°, and for the thermal expansion the expression

$$V = 1 + \cdot 0_3 86172\, t + \cdot 0_5 25344\, t^2 - \cdot 0_8 18319\, t^3,$$

given by WEGER (' Annalen,' vol. 221, p. 67).

On plotting the above values the coefficients (II.) contained in the third column of the following table were obtained. The second column gives the coefficients (I.) found from the original sample of ethyl benzene, and the differences between the two series of values are given in the last column.

Temp.	η.		Difference.
	I.	II.	
0°	·00874	·00874	00000
10	·00758	·007575	·000005
20	·006665	·00665	·000015
30	·00592	·00590	·00002
40	·00529	·005265	·000025
50	·00477	·00474	·00003
60	·00432	·00429	·00003
70	·00394	·00391	·00003
80	·00360	·003575	·000025
90	·003305	·003285	·00002
100	·003045	·00303	·000015
110	·002815	·002805	·00001
120	·00262	·00261	·00001
130	·002435	·002425	·00001

At low temperatures the values are identical, and at high temperatures the new sample gives coefficients which are the lower by about 0·4 per cent. Between 30°

and 90° the differences reach a maximum, but never amount to more than 0·7 per cent. The conclusions based upon the coefficients η given by the original sample remain, therefore, unaltered, and we do not think it necessary to deduce a new formula of the Slotte type to reproduce the values given by sample No. 2; because, when the temperature range is so extended as 130°, the average difference between calculated and observed values is as great as the above differences between the coefficients of the two samples. The formula already given for ethylbenzene, although derived from the values for sample No. 1, may still be taken to give values as near the truth as it is possible to obtain by means of a formula of the Slotte type from the coefficients given by sample No. 2.

GRAPHICAL REPRESENTATION OF RESULTS.

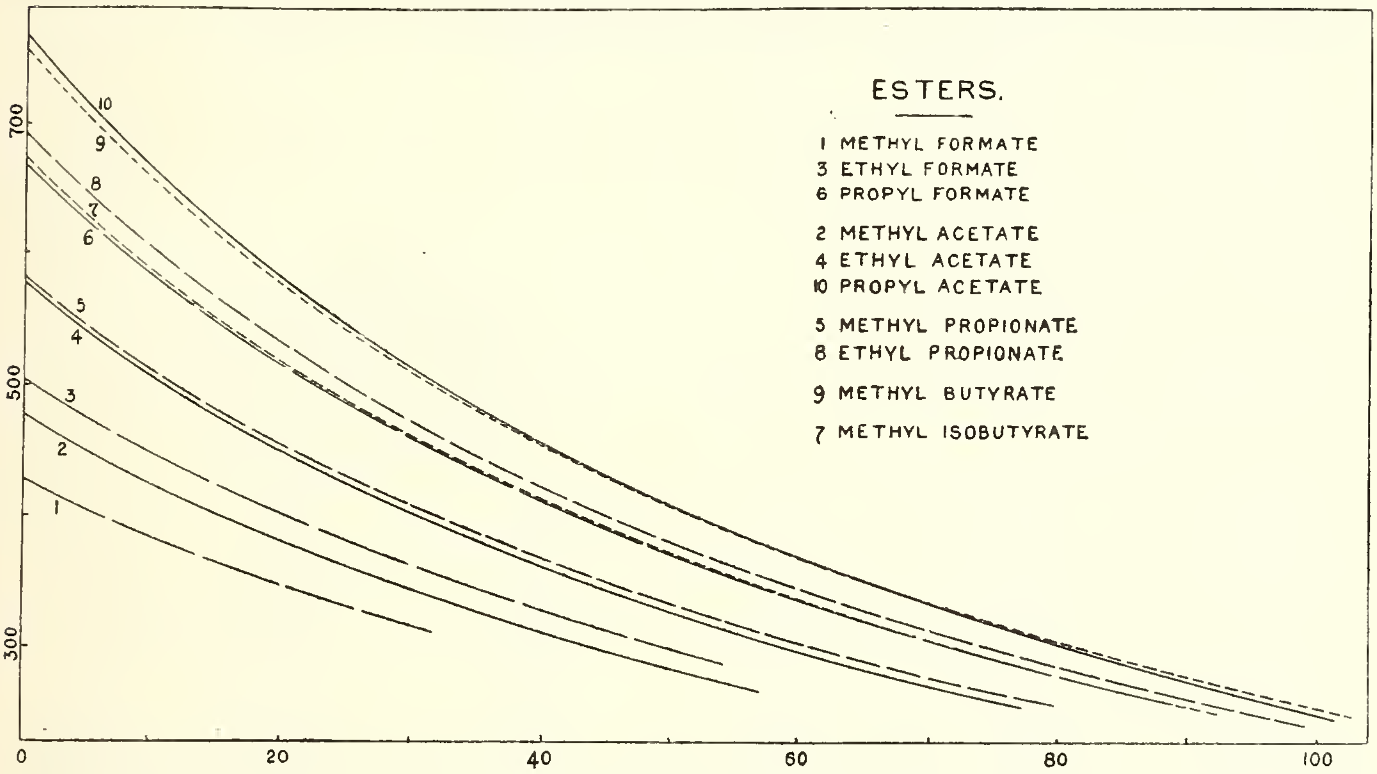
The relative position of the viscosity-curves of different members of the series of esters and ethers is shown in the following figures. The ordinates are viscosity-coefficients multiplied by 10^5, and the abscissæ are temperatures.

Esters (fig. 1).

The esters investigated were the three lowest formates, the three lowest acetates, the three lowest propionates, methyl butyrate, and methyl isobutyrate. Fig. 1 represents the curves obtained. The first noteworthy point in connection with the curves is, that in all cases their slope is comparatively small, and varies but little with the temperature. In this respect the esters differ to a most marked extent from the acids and alcohols from which they are derived, since one of the characteristic features of these two classes of compounds was the large effect exerted by temperature upon viscosity, and the large extent to which this effect altered as the temperature altered. The behaviour of the esters, therefore, is a further argument in support of our conclusion that the presence of the hydroxyl-group is the main cause of the exceptional course of the curves for the acids and alcohols, for it proves that when by the mutual interaction of an acid and alcohol the hydroxylic nature of both is destroyed, the resulting compound gives a curve in no way resembling those of the reacting substances. Indeed, the curves for the esters resemble in shape those of non-associated liquids in general; they give no indication of the presence of molecular aggregates. This is, of course, in harmony with the mass of physical evidence, which goes to show that, with very few exceptions, hydroxy-liquids alone contain molecular aggregates.

As regards the disposition of the curves, it has to be noted, in the first place, that according to the general rule obeyed in homologous series of simple liquids, they follow one another in the order of the molecular weights of the esters. Passing along the diagram from below upwards we have, first, the curve for methyl formate, then the curves for its next higher homologues, the isomers methyl acetate and ethyl formate; then come the curves for the next higher homologues, the isomers ethyl acetate, methyl propionate, and propyl formate; and, lastly, the curves for the next higher isomeric homologues methyl isobutyrate, ethyl propionate, methyl butyrate, and propyl acetate. Passing to the relative position of the curves for isomeric esters, it is noticeable that, where the comparison is possible, the formate has at any temperature, the largest viscosity-coefficient. The curve for ethyl formate lies to the right of that for methyl formate, and the curve for propyl formate is far to the right of those for ethyl acetate and methyl propionate; indeed, at low temperatures it

Fig. 1.



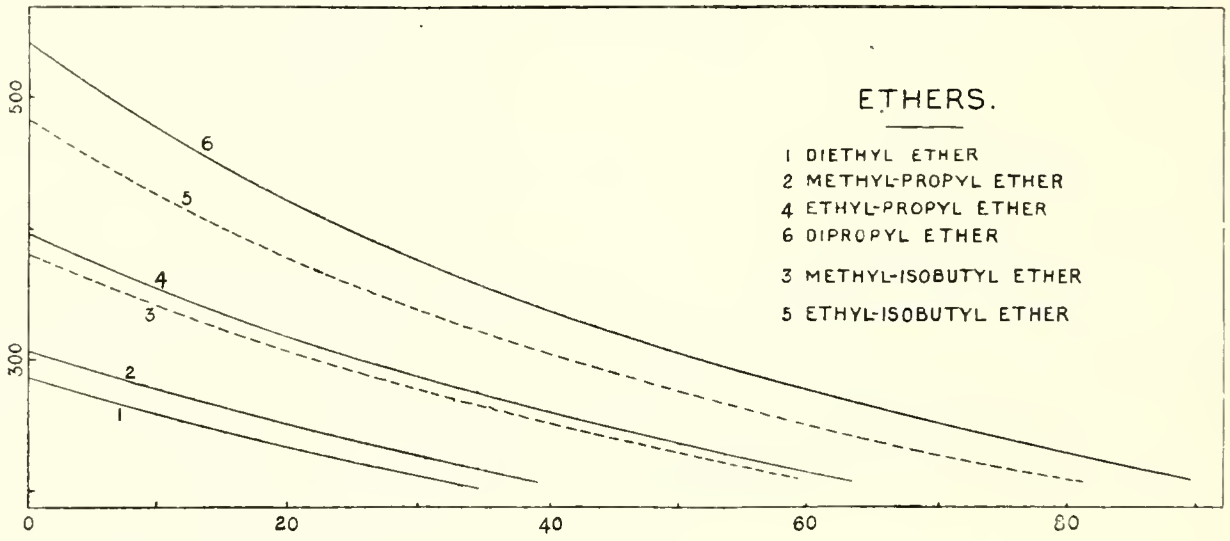
almost coincides, and at high temperatures it actually coincides, with the curve of its higher homologue, methyl isobutyrate. It is more than likely that the large viscosity-coefficients of the formates are associated with the fact, previously established, that of the five lowest fatty acids, formic acid has, at low temperatures, the largest coefficients, and that these coefficients are larger than they might be expected to be even on making allowance for molecular aggregation.

On comparing the isomeric propionates and acetates, it is seen that although the curve for ethyl acetate is very slightly to the left of that for methyl propionate, the curve for propyl acetate is far to the right of that for ethyl propionate. This is the result of the influence exerted by the symmetry of the molecule in lowering the viscosity. In the first case the acetate is a symmetrical compound and the propionate is unsymmetrical; in the second case both compounds are unsymmetrical. In conformity with the general rule, the curve for methyl isobutyrate lies well to the left of that of methyl butyrate—it is, indeed, to the left of those of any of its isomers. The curves of methyl butyrate and propyl acetate are interesting inasmuch as, contrary to what holds in most series of related substances, they cut one another. At 0° the coefficient of the acetate is the larger by about 1·4 per cent., while at 100° the coefficient of the butyrate is the larger by about 2·4 per cent.

Ethers.

Five ethers have been dealt with in the previous part of this paper. The curves obtained are given in fig. 2, which also contains, for the sake of comparison, the curve for ethyl ether. As in the case of the esters, the effect of temperature on viscosity is small, and does not vary much as the temperature alters.

Fig. 2.



On passing along the diagram from below upwards the order of the curves is: diethyl ether, methyl propyl ether, methyl isobutyl ether, ethyl propyl ether, ethyl isobutyl ether, and dipropyl ether. They follow, therefore, in the order of the molecular weights of the compounds.

As regards the curves of isomers, it is noticeable that diethyl ether, the symmetrical isomer, has at all temperatures a lower viscosity than methyl propyl ether.

Again, as in the case of esters, of the isomeric ethers the iso-compound has the lowest viscosity; the curve for methyl isobutyl ether lies below that of ethyl propyl ether, and the curve for ethyl isobutyl ether lies below that of the symmetrical isomer dipropyl ether. This last comparison is interesting as showing that the presence of an iso-linkage has a more important effect in reducing the viscosity than the mere symmetry of the molecule.

In our previous paper an effect of symmetry similar to that which holds for the esters and ethers was shown by diethyl and methyl propyl ketones; the symmetrical isomer had the lowest viscosity.

The following tables contain the coefficients of viscosity read off from the working curves at intervals of 10°. Similar values for the new samples of isopentane and ethyl benzene have already been given on pp. 89 and 91 respectively.

Coefficients of Viscosity (Dynes per sq. centim.).

Esters.

Temp.	Methyl Formate.	Ethyl Formate.	Propyl Formate.	Methyl Acetate.	Ethyl Acetate.
0°	·00429	·00505	·00668	·00478	·00578
10	·00384	·00448	·00584	·00425	·00507
20	·00347	·00402	·00516	·00381	·00449
30	·00317	00362	·00459	·00344	·00401
40	..	·00328	·00411	·00312	·00360
50	..	·002995	·00371	·00284	·00326
60	..	..	·003365	..	·002965
70	..	..	·003065	..	·00270
80	..	..	·00280		..

Temp.	Propyl Acetate.	Methyl Propionate.	Ethyl Propionate.	Methyl Butyrate.	Methyl Isobutyrate.
0°	·00770	·00582	·00693	·00759	·006725
10	·006655	·00512	·00604	·00657	·00587
20	·00581	·00454	·00532	·00575	·00518
30	·00511	·00408	·00472	·00508	·00461
40	·00455	·00368	·004225	·00453	·00413
50	·00408	·00334	·003805	·00407	·00372
60	·003675	·00304	·00345	·003675	·003375
70	·003335	·002775	·003135	·00334	·00307
80	·003035	..	·00286	·00304	·00280
90	·00276	..	·00262	·00278	·00256
100	·00250	..	..	·00256	..

Ethers.

Temp.	Methyl Propyl Ether.	Ethyl Propyl Ether.	Dipropyl Ether.	Methyl Isobutyl Ether	Ethyl Isobutyl Ether.
0°	·00307	·003965	·00540	·00381	·00482
10	·00277	·00354	·00474	·00340	·00425
20	·002515	·003175	·00420	·003065	·003785
30	·00228	·002865	·00375	·00277	·00339
40	..	·00260	·003375	·00252	·003045
50	..	·00237	·003045	·00230	·002765
60	..	·002165	·00277	..	·00251
70	..	..	·00252	..	·00229
80	..	..	·00231	..	·002105

Conclusions relating to the Graphical Representation of the Results.

Both ethers and esters give no evidence of molecular aggregation and conform to the rules that—

(1.) In homologous series the viscosity is greater the greater the molecular weight.

(2.) An iso-compound has a smaller viscosity then a normal isomer.

(3.) The more symmetrical the molecule of an isomeric compound the lower is the viscosity.

As regards the esters themselves it is noteworthy, where the comparison has been made, that—

(4.) Of isomeric esters the formate has the largest viscosity.

ALGEBRAICAL REPRESENTATION OF THE RESULTS.

The following table gives the values of the constants in SLOTTE'S formula for the esters and ethers. Here the formula is written in the shape $\eta = C/(1 + bt)^n$ instead of that already used, viz., $\eta = C/(a + t)^n$. C is, of course, the value of η at 0°, and since, in general, the curves do not cross one another, relationships exist between the values of C for the different substances similar to those just discussed and which hold regarding the position of the viscosity curves.

CONSTANTS in SLOTTE'S formula $\eta = C/(1 + bt)^n$.

	C.	*b*.	*n*.
Methyl formate	·004301	·014655	0·8325
Ethyl formate	·005048	·007197	1·7006
Propyl formate	·006679	·007179	1·9154
Methyl acetate	·004781	·006472	1·8636
Ethyl acetate	·005783	·007384	1·8268
Propyl acetate	·007706	·007983	1·8972
Methyl propionate	·005816	·006820	1·8972
Ethyl propionate	·006928	·007468	1·8914
Methyl butyrate	·007587	·008081	1·8375
Methyl isobutyrate	·006720	·007144	1·9405
Diethyl ether	·002864	·007332	1·4644
Methyl propyl ether	·003077	·006809	1·5863
Ethyl propyl ether	·003969	·005454	2·1454
Dipropyl ether	·005401	·006740	1·9734
Methyl isobutyl ether	·003813	·005737	2·0109
Ethyl isobutyl ether	·004826	·006549	1·9733

Since the values of *n* and *b* are interdependent, their individual magnitudes need not show any definite relationships to the chemical nature of the substances. It is easy to prove, however, by the method already adopted, that the temperature coefficients are in reality closely related to chemical nature. If the denominator of the left-hand side of the equation $\eta = C/(1 + bt)^n$ be expanded, and if terms involving higher powers of t than t^2 be neglected, we obtain an expression of the shape $\eta = C/(1 + \beta t + \gamma t^2)$. Such an expression closely reproduces the observed values of esters and ethers. This is shown in the following table, which also gives the values of β and γ.

FORMULA $\eta = C\,(1 + \beta t + \gamma t^2)$.

	β.	γ.	t.	$\eta \times 10^5$ (Calc.).	$\eta \times 10^5$ (Obs.).	Diff. $\times 10^5$.
Methyl formate	·01220	−0·1497	30°	318	317	−1
Ethyl formate	·01224	0·3086	50	299	299	0
Propyl formate	·01375	0·4519	80	280	280	0
Methyl acetate	·01206	0·3370	50	283	284	1
Ethyl acetate	·01349	0·4117	70	269	270	1
Propyl acetate	·01514	0·5423	100	252	250	−2
Methyl propionate . . .	·01294	0·3958	70	277	277	0
Ethyl propionate . . .	·01412	0·4701	90	261	261	0
Methyl butyrate	·01485	0·5025	100	254	256	2
Methyl isobutyrate . . .	·01386	0·4657	90	256	256	0
Diethyl ether	·01074	0·1828	30	214	212	−2
Methyl propyl ether . .	·01080	0·2156	30	229	228	−1
Ethyl propyl ether . . .	·01170	0·3655	60	216	216	0
Dipropyl ether	·01330	0·4363	80	231	231	0
Methyl isobutyl ether . .	·01154	0·3345	50	230	230	0
Ethyl isobutyl ether . .	·01292	0·4119	80	209	210	1

The last four columns in the table go to show that even at high temperatures where, from its mode of derivation the formula should be least satisfactory, it gives values agreeing closely with those observed. Under t is given a temperature near the boiling-point of the liquid; under (calc.) and (obs.), the calculated and observed values, respectively, of the viscosity-coefficients at t, and the difference between the values is given in the last column. It is clear that in all cases a formula of the above type will closely reproduce the observed values of η, and, consequently, β and γ may be regarded as the temperature-coefficients of the different substances. It will be seen from the table that the magnitudes of β and γ are closely related to chemical composition. From the fact that the value of n for methyl formate happens to be less than unity, the value of γ for this ester is negative, and hence its coefficients cannot be satisfactorily compared with those of the other substances, as they are all positive. Excluding methyl formate, the table shows that in general—

(1.) In any homologous series β and γ increase as the molecular weight increases.

(2.) Of isomeric compounds the iso-compound has the smallest coefficients.

(3.) Ethyl ether, the symmetrical isomer, has smaller coefficients than methyl propyl ether.

(4.) As regards normal isomeric esters, the formate has the largest and the propionate the smallest coefficients, and the values of the acetate are larger than of the butyrate.

COMPARISON OF VISCOSITY MAGNITUDES AT COMPARABLE TEMPERATURES.

In what follows we deal with the relationships which exist between the various viscosity magnitudes—the viscosity-coefficient, the molecular viscosity, and the molecular viscosity work—first, at the boiling-point, and, second, at temperatures of equal slope, the slope adopted being that employed in our previous paper, viz., $0{\cdot}0_4323$.

A. COMPARISON of Viscosity Magnitudes at the Boiling-point.

Esters.

	Viscosity-Coefficients. η in dynes per sq. centim. × 10^5.			Molecular Viscosity. η in dynes per sq. centim. × specific molecular area in sq. centims. × 10^4.			Molecular Viscosity Work. η in dynes per sq. centim. × specific molecular vol. in cub. centims. × 10^3.		
	Methyl.	Ethyl.	Propyl.	Methyl.	Ethyl.	Propyl.	Methyl.	Ethyl.	Propyl.
Formate . .	312	289	278	492	555	620	195	243	293
Acetate . .	266	253	246	508	567	626	222	268	315
Propionate .	255	242	..	565	614	..	266	309	..
Butyrate . .	250	..	..	630	..	..	317	..	..
Isobutyrate .	251	..	..	633	..	..	318	..	..

Ethers.

	Viscosity-Coefficients. η in dynes per sq. centim. × 10^5.	Molecular Viscosity. η in dynes per sq. centim. × specific molecular area in sq. centims. × 10^4.	Molecular Viscosity Work. η in dynes per sq. centim. × specific molecular vol. in cub. centim. × 10^3.
Methyl propyl .	211	471	222
Ethyl propyl . .	210	534	269
Dipropyl . . .	212	601	320
Diethyl . . .	205	459	217
Methyl isobutyl	210	534	269
Ethyl isobutyl .	208	593	316

As regards the esters, it will be seen that the different series follow the rule obeyed in most homologous series, viz., that the viscosity-coefficients diminish as the molecular weight increases. All the differences are negative, and diminish as a series is ascended.

Of the isomeric butyrates the iso-compound, in conformity with the general rule (compare p. 599, Part I.), has the larger coefficient. The ethers, however, afford an additional instance of an homologous series (compare pp. 590 and 592, Part I.) in which the different members have nearly the same viscosity at the boiling-point. On comparing the values for diethyl ether and methyl propyl ether the symmetrical compound, as in the case of the ketones (compare pp. 599 and 605, Part I.) has the lower viscosity.

The exceptional character of the formates is no doubt connected with the exceptional behaviour of formic acid, the molecular viscosity of which is abnormally large, greater, indeed, than that of acetic acid (compare pp. 591 and 610, Part I.).

In our previous paper we showed that the values of CH_2 varied in different series, but that on making allowance for the influence of molecular complexity and of differences in chemical constitution (compare p. 606, Part I.), we concluded that the probable value of the effect of CH_2 on the molecular viscosity of comparable liquids was 62. It is satisfactory to find that this number is almost identical with the mean value now given by the esters and ethers, as derived from the thirteen available differences, viz., 61 ± 6.

As regards molecular viscosity work it will be seen that the differences between the formates and acetates are nearly constant and in mean about 25; whilst the remaining differences given by the esters are also fairly uniform, viz., 46, the mean value given by the ethers is 50. The general mean, 48 ± 3, corresponds with that arrived at in our former paper, viz., 47.

The Value of Ether Oxygen.—Since the effect of CH_2 on the molecular viscosity and molecular viscosity work of the esters and ethers is the same as the value adopted in our previous paper, we may assume that the values of the atomic constants of carbon and hydrogen there used also apply in the case of the esters and ethers. If we further assume that the value of carbonyl oxygen is the same for the ethers as for the ketones, we have all the data for calculating the value of ether oxygens. The results are given in the following tables:—

Esters.

	$C_nH_{2n}\overset{\|}{O}O<$. ηd^2 (Obs.).	$C_nH_{2n}\overset{\|}{O}$. (Calc.).	$O<$.
Methyl formate	492	372	120
Ethyl formate	555	434	121
Propyl formate	620	496	124
Methyl acetate	508	434	74
Ethyl acetate	567	496	71
Propyl acetate	626	558	68
Methyl propionate	565	496	69
Ethyl propionate	614	558	56
Methyl butyrate	630	558	72
Methyl isobutyrate	633	573	60

Ethers.

	$C_nH_{2n+2}O<$. ηd^2 (Obs.).	C_nH_{2n+2}. (Calc.).	$O<$.
Diethyl	459	408	51
Methyl propyl	471	409	63
Ethyl propyl	534	470	61
Dipropyl	601	532	69
Methyl isobutyl	534	485	49
Ethyl isobutyl	593	547	46

As regards both molecular viscosity and molecular viscosity work, the formates—as was to be expected from what has been already stated—give values which are much larger than those of other compounds. Of the remaining liquids the general mean of the values of ethers and esters as regards molecular viscosity is 62 ± 8. The variations of the individual values are no doubt large, arising mainly from the fact that in the case of normal isomers the same calculated value is deducted from the observed numbers, no regard being paid to the effect of symmetry of the molecule, etc., on the viscosity. A quantitative measure of these effects will only be possible after a much larger number of compounds has been investigated. There can, however, be no question of the large differences which exist between the atomic constants of hydroxyl oxygen, carbonyl oxygen, and ether oxygen.

Taking the value found above, we may now write as the probable values of oxygen in the three different conditions—

	Molecular Viscosity.	Molecular Viscosity Work.
Hydroxyl oxygen	196	102
Carbonyl oxygen	248	41
Ether oxygen	62	37

These numbers, of course, can only be regarded as provisional; they are mainly put forward as confirming the conclusion already indicated in our previous paper, that the constitution of oxy-compounds largely affects their viscosity.

B. Comparison of Viscosity Magnitudes at Temperatures of Equal Slope.

Esters.

	Viscosity-Coefficients. η in dynes per sq. cm. $\times 10^5$.			Molecular Viscosity. η in dynes per sq. cm. $\times$ specific mol. area, in sq. cm. $\times 10^4$.			Molec. Viscosity Work. η in dynes per sq. cm. $\times$ specific mol. vol., in cb.c. $\times 10^3$.		
	Methyl.	Ethyl.	Propyl.	Methyl.	Ethyl.	Propyl.	Methyl.	Ethyl.	Propyl.
Formate	345	336	336	538	635	734	212	276	344
Acetate	328	327	333	613	713	822	265	333	408
Propionate	334	336	. .	720	822	. .	334	407	. .
Butyrate	338	. .	. .	826	. .	. .	408	. .	. .
Isobutyrate	335	. .	. .	819	. .	. .	405	. .	. .

Ethers.

	Viscosity-Coefficients. η in dynes per sq. cm. $\times 10^5$.	Molecular Viscosity. η in dynes per sq. cm. $\times$ specific mol. area, in sq. cm. $\times 10^4$.	Molec. Viscosity Work. η in dynes per sq. cm. $\times$ specific mol. vol., in cb.c. $\times 10^3$.
Methyl propyl. . . .	302	648	300
Ethyl propyl	310	755	373
Dipropyl	318	865	451
Diethyl	295	635	295
Methyl isobutyl . . .	311	757	374
Ethyl isobutyl	312	849	444

It will be seen, in the case of both esters and ethers, that the viscosity-coefficients at temperatures of equal slope are fairly concordant amongst themselves, and tend, in the case of the ethers, to become larger with increase of molecular weight. In the case of the ethers—diethyl and methyl propyl—the symmetrical compound, under all conditions of comparison, has the smaller value; in this respect the ethers resemble the ketones.

As in the case of the comparisons at the boiling-point, the formate has a larger molecular viscosity than any of the isomers (compare ethyl formate and methyl acetate; propyl formate and ethyl acetate)—another indication of the specific influence exerted by the formyl group. The values of other normal esters obey the rule that the more nearly the number of carbon atoms in the acid radicle approximates to the number in the alcohol radicle the lower is the molecular viscosity. Methyl isobutyrate gives a smaller value than methyl butyrate; a similar result was found in the case of six comparisons in our previous paper.

In any group of normal isomeric esters, the formate has the largest value of molecular viscosity work (compare ethyl formate with methyl acetate; propyl formate with ethyl acetate). The other members of the group have values which are practically identical (ethyl acetate 333, methyl propionate 334 ; propyl acetate 408, ethyl propionate 407, methyl butyrate 408. Methyl isobutyrate follows the general rule in giving a smaller value than the methyl butyrate.

Values for ether oxygen at temperatures of equal slope have been calculated using the values given in our previous paper for CH_2 and carbonyl oxygen, but it is evident that the values afforded by the esters are not independent of molecular weight, as they diminish, without exception, as any series of esters is ascended. Moreover, it is not possible to allow for the fact already noted that the molecular viscosity of an isomeric ester is the smaller the more nearly the number of carbon atoms in the acid radicle approximates to the number in the alcohol radicle. The main result, however, comes out as clearly as in the first condition of comparison that ether oxygen has invariably an effect on molecular viscosity widely different from the effects of hydroxyl oxygen and carbonyl oxygen. Thus, in the case of molecular viscosity, the values obtained were—

Hydroxyl oxygen	166
Carbonyl oxygen	198
Ether oxygen	51

Although these numbers can only be considered as first approximations, they clearly indicate, as already stated, that the constitution of oxy-compounds profoundly affects their viscosity.

The following table shows the temperature at which the viscosity curves have the slope $\cdot 0_4323$:—

Esters.

	Methyl.	Ethyl.	Propyl.
Formate	20°·7	37°·7	60°·1
Acetate	34·7	49·6	69·9
Propionate	49·7	62·6	. .
Butyrate	68·5	. .	. .
Isobutyrate	60·7	. .	. .

Ethers.

Methyl propyl	1°·6
Ethyl propyl	22·4
Dipropyl	45·8
Diethyl	−2·7
Methyl isobutyl	18·7
Ethyl isobutyl	37·8

It will be noticed that in all cases an increment of CH_2 brings about an increase in the temperature of equal slope, and in all cases the increase becomes greater as the series is ascended. In any group of normal isomers the formate has the largest temperature value and, with the possible exception of ethyl propionate, the remaining esters in the group have almost the same value. According to the general rule, methyl isobutyrate has a lower value than methyl butyrate, and, as in the case of the ketones, of the two ethers, diethyl and methyl propyl, the symmetrical isomer has the lower equal-slope temperature.

Appendix.

On the Preparation of Ethers. By R. E. Barnett, *B.Sc., Assoc. R.C.S.*

The ethers prepared and used for viscosity observations were methyl propyl, ethyl propyl, dipropyl, methyl isobutyl, and ethyl isobutyl.

The most rapid and economical method of preparing certain ethers is undoubtedly the "continuous etherification" of alcohols by means of sulphuric acid, first used by Boullay and investigated by Williamson. Although it has been shown, originally by Williamson ('Annalen,' 81, 77) and later by Norton and Prescott ('Amer. Chem. Journ.,' 6, 241), that this method is applicable to the preparation of mixed ethers, there are always formed, as would be expected, considerable quantities of the two possible simple ethers containing the same alkyl radicles. The great difficulty of separating any one ether from such a mixture, and the absence of any certain chemical method of ascertaining the presence of isomers, render this method particularly unsuitable for preparing ethers for physical investigation. The liability of the higher fatty alcohols to oxidation by the sulphuric acid, which limits the application of this method to alcohols containing not more than three carbon atoms (Norton and Prescott, *loc. cit.*), is partially obviated by the employment of the sulphonic acids of benzene, naphthalene, and similar compounds (Krafft, 'Berichte,' 26, 2829).

Although it is evident that the *à priori* objections mentioned above apply equally to this method, it was tried in preparing dipropyl ether. Employing benzenesulphonic acid, a liberal supply of which we owe to the kindness of Messrs. Brooke, Simpson, and Spiller, considerable difficulty was found in getting anything like complete etherification. Much propyl alcohol always came over with the ether, and as their boiling-points only differ by some seven degrees, the mixture was difficult to separate by fractionation. A better result was obtained by passing the first product through the acid again, but still much alcohol was present. After a rough separation, the ether was repeatedly treated with sodium wire, until further action practically ceased. The resulting product was fractionated four times in a Lebel-Henninger apparatus. It was evidently a mixture, containing presumably also di-isopropyl and propyl isopropyl ethers. The total range of boiling-point was from 85° to 90° (uncor.), while the boiling-point of dipropyl ether is 90°·7 (ZANDER, 'Annalen,' 214, 163). This product showed, as far as distillation can show, the presence of far greater proportions of isomeric compounds than the mixed ethers prepared from the same propyl alcohol in the manner presently to be described; this appears to confirm the view expressed above of the tendency to the formation of mixed ethers in these processes, and the consequent augmentation of the proportions of isomeric compounds present in the alcohol employed. The preparation of di-isobutyl ether by this process was also attempted by using naphthalene sulphonic acid, but the difficulty of complete etherification and the very impure product formed caused the process to be abandoned.

Excluding the method depending upon the action of silver oxide upon alkyl iodides (ERLENMEYER, 'Annalen,' 126, 306; LINNEMANN, 'Annalen,' 161, 37), the only other available processes are those based upon the condensation of alcohol with alkyl halides in the presence of an alcoholate or hydroxide of an alkyl metal, or of triethylamine. The last-named substance was employed by REBOUL ('Compt. Rend.,' 93, 69). As his method involves the use of sealed tubes, and does not prevent the formation of olefine, it was not tried.

The method described by CHANCEL ('Compt. Rend.,' vol. 68, p. 726; 'Annalen,' vol. 151, p. 305), and previously used by BALARD, has the advantage of dispensing with metallic sodium, and has consequently been frequently employed. CHANCEL prepared methyl, ethyl, propyl, and amyl propyl ethers by acting upon a mixture of propyl alcohol and powdered caustic potash with the alkyl iodide. The formation of the dipropyl ether, which is the only one fully described, was attended with the production of much propylene, especially in the presence of excess of alkali. The boiling-points given are so widely different from those of DOBRINER and other subsequent investigators that CHANCEL'S ethers must have been very impure, probably from the presence of undecomposed iodide. LIEBEN and ROSSI ('Annalen,' vol. 158, p. 167) tried CHANCEL'S process, using butyl iodide with caustic potash and ethyl alcohol, and found that two-thirds of the iodide was converted into ethyl-butyl ether. SAYTZEW ('Journ Prakt. Chem.,' (2), vol. 3, p. 88), using the same substances and a similar method obtained an amount of butylene representing about one-fourth of the iodide employed. MARKOWNIKOFF ('Annalen,' vol. 138, p. 374), obtained ethyl isopropyl ether as a bye-product in the action of potassium cyanide in alcoholic solution upon isopropyl iodide. He observed that the amount of ether produced increased with the strength of alcohol employed, reaching the maximum with absolute alcohol.

In trying this method, roughly-powdered caustic potash was added to propyl alcohol in a flask, and after cooling, ethyl iodide was poured in. The mixture was warmed on a water-bath under a reflux condenser; the action rapidly became very vigorous, and a considerable quantity of gas was evolved. After some time, when the reaction appeared to be complete, the liquid portion was distilled off and treated with calcium chloride. It boiled entirely between 63° and 68°. On treatment with sodium it became evident that this product contained a very large quantity of undecomposed ethyl iodide, and it was found practically impossible to purify it by any means short of further etherification. In a second experiment more alkali was used, and in this case the mixture of propyl alcohol and caustic potash was kept hot, and ethyl iodide added through the reflux condenser at intervals. Gas was still given off, and the product obtained again boiled between the same limits and contained much iodide.

It will be seen that the disadvantage of CHANCEL'S method is that the large quantity of caustic alkali converts much of the alkyl iodide into olefine, while, on the other hand, unless a great excess of potash is used, the product contains undecomposed iodide.

Although an alcoholic solution of caustic alkali is stated to contain a large proportion of alcoholate, yet the other method, in which the alkali metal is dissolved in the pure alcohol, differs very markedly from CHANCEL'S, and, as will be seen from the experiments presently to be described, is greatly superior as a quantitative method for the preparation of ethers. This does not, however, immediately appear from the existing records. BRÜHL ('Annalen,' vol. 200, p. 177) acted upon sodium ethoxide in alcoholic solution with propyl bromide; he found propylene evolved, and the yield of ether low. ZANDER ('Annalen,' vol. 214, p. 163) employing sodium propylate with propyl iodide, obtained only a 25 per cent. yield of dipropyl ether. By the use of solid sodium ethoxide and butyl bromide, LIEBEN and ROSSI obtained ethyl butyl ether as chief product, with a small quantity of butylene; but this experiment was performed in a sealed tube and is consequently not quite comparable. It is noteworthy, however, that only 1·5 times the theoretical quantity of the ethoxide was used, while to decompose the less stable butyl iodide SAYTZEW (*loc. cit.*) had to use six times the calculated amount of potassium hydroxide in CHANCEL'S process.

A careful comparison of all the above-mentioned results with others by BALARD, GUTHRIE, and WILLIAMSON, has led, in the light of experiments described below, to conclusions which may be stated as follows; they refer to the preparation of ethers containing alkyl radicles from methyl to amyl inclusive.

i. The action of a solution of sodium in an anhydrous alcohol upon an alkyl halide tends quantitatively to the production of an ether,* and differs markedly from the action of an alcoholic solution of an alkaline hydroxide.

ii. In preparing mixed ethers by this reaction, the halogen-derivative should contain the alkyl radicle of lower molecular weight, the reaction then being apparently the more simple and regular, and the yield better the greater the difference between the two alkyls.

iii. Where the use of the halogen-derivative of propyl or a higher alkyl becomes unavoidable, the bromide, or sometimes the chloride, should be substituted for the iodide.

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* *Cf.* HECHT and CONRAD ('Zeits. Physik. Chem.,' 3, 450), on this reaction.

The second of these conclusions finds some support in the work of SILVA ('Compt. Rend.,' 81, 323), who showed that when a mixed ether is decomposed by hydriodic acid the higher radicle becomes an alcohol and the lower an iodide.

Although the rule given may seem obvious in view of the known instability of the higher alkyl iodides, it is shown above that in practice it has been generally disregarded. A possible reason for this is the increasing difficulty of dissolving sodium as we ascend the series of alcohols. In the work recorded below, it was not found possible in any reasonable time to dissolve more than one molecular proportion of sodium in two or three of propyl or isobutyl alocohols. The consequent waste of alcohol may be obviated by the use of the following continuous process, by means of which the conversion of alkyl iodides and alcoholates into ether can be carried out in almost theoretical proportions.

A WURTZ flask of about a litre capacity has the side-tube (which should be nearly at right angles to the neck) lengthened to about a metre, and this surrounded by the outer tube of a condenser for nearly its whole length to secure efficient condensation. The flask is placed on a water-bath, and by inclining it until the condenser slopes upward at some 30° with the horizontal we have a reflux apparatus, while a simple rotation through 60° downwards adapts it for distillation.

Placing it with the condenser sloping upwards, 150 grams of the alcohol (propyl or isobutyl) is introduced through the neck, which is fitted with an easily-removable cork. A clean dry bottle, wide mouthed and stoppered, is tared, and about 30 grams of clean sodium put into it. It is again weighed, so that at any time the amount used can be ascertained; if dry and well-stoppered, oxidation is only superficial. Some pieces are cut off and introduced into the flask; it dissolves rapidly at first with evolution of heat. More sodium is added at intervals, taking care not to use more than can be dissolved within a reasonable time; say 20 to 22 grams for 150 grams alcohol. The water-bath is heated, as if the solution be allowed to cool it solidifies. Directly the sodium has dissolved, the cork in the neck is replaced by one carrying a bent tap-funnel, in which the iodide (methyl or ethyl) is placed. This is allowed to flow in small portions into the thick liquid; the flask is gently rotated to prevent the heavy iodide sinking to the bottom and causing violent bumping, and in a moment the whole mass becomes clouded by the separation of sodium iodide. The whole of the iodide is gradually added in this way, the amount being that calculated for three-fourths of the sodium present. With this proportion, though but little more than equimolecular, there was never a trace of iodide in any of the distillates.

After a short digestion the condenser is turned down without interrupting the boiling, and the ether distils over. It is accompanied with but little alcohol, possibly on account of the alcoholate still in solution raising the boiling-point. Directly the distillation slackens, the condenser is turned up again, and more sodium introduced; a further quantity of ten or twelve grams can be dissolved in the remaining alcohol. An amount of alkyl iodide, three-fourths of that required for the total quantity of sodium alcoholate now in the flask, is added as before, and so a second quantity of ether obtained. It is possible to continue this process so that the final amounts of sodium and alcohol unutilised shall bear as small a proportion to the total ether produced as we please, especially if the alcohol obtained by fractionation of the early distillates be added to the flask; but time and the accumulation of sodium iodide fix a practical limit.

The ethers prepared in this way were methyl-propyl, ethyl-propyl, methyl-isobutyl, and ethyl-isobutyl. The dipropyl ether was prepared by KRAFFT's method, as already described. The methyl and ethyl iodides used were prepared by myself. The alcohols were obtained from KAHLBAUM; the propyl alcohol boiled between 95°·7 and 97°·0 (corr.), and the isobutyl alcohol from 106°·4 to 108° (corr.). Each ether was repeatedly fractionated in a LEBEL-HENNINGER apparatus, and the main fraction, after frequent and prolonged digestion with sodium wire, boiled within about half a degree. It appeared to be practically impossible to obtain an ether which would show absolutely no gas bubbles on the introduction of fresh sodium wire, so one was compelled to consider the drying complete when the amount of this trifling action became constant on each successive addition of wire. This minute quantity of moisture would appear to have no effect upon the viscosity observations, as an ether after repeated treatment with phosphoric oxide gave results almost identical with those given by the liquid before treatment. (See p. 83.)

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IV. *On the Capacity and Residual Charge of Dielectrics as Affected by Temperature and Time.*

By J. Hopkinson, *F.R.S.*, *and* E. Wilson.

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Before describing the experiments* forming the principal subject of this communication, and their results, it may be convenient to shortly state the laws of residual charge.

Let x_t be the potential at any time t of a condenser, *e.g.*, a glass flask, let y_t be the time integral of current through the flask up to time t, or, in other words, let y_t be the electric displacement, including therein electric displacement due to ordinary conduction. If the potential be applied for a short time ω, let the displacement at time t, after time ω has elapsed from the application of force $x_{t-\omega}$ be $x_{t-\omega}\,\psi(\omega)\,d\omega$; this assumes that the effects produced are proportional to the forces producing them; that is, that we may add the effects of simultaneously-applied electromotive forces. Generalise this to the extent of assuming that we may add the effects of successively-applied electromotive forces, then $y_t = \int_0^\infty x_{t-\omega}\,\psi(\omega)\,d\omega$. This is nothing else than a slight generalisation of Ohm's Law, and of the law that the charge of a condenser is proportional to its potential. Experiments were tried some years ago for the purpose of supporting this law of superposition as regards capacity. It was shown that the electrostatic capacity of light flint glass remained constant up to 5,000 volts per millimetre ('Phil. Trans.,' 1881, Part II., p. 365). The consequences of deviation from proportionality were considered ('Proc. Roy. Soc.,' 1886, vol. 41, p. 453), and it was shown that, if the law held, the capacity as determined by the method of attractions was equal to that determined by the method of condensers; this is known to be the case with one or two doubtful exceptions (*ibid.*, p. 458). Rough experiments have been made to show that residual charge is proportional to potential; they indicate that it is ('Phil. Trans.,' vol. 167, Part II.). The integral $y_t = \int_0^\infty x_{t-\omega}\,\psi(\omega)\,d\omega$ includes in itself ordinary conduction, residual

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* These experiments were commenced in the summer of 1894, and we have to thank Messrs. C. J. Evans and R. E. Shawcross for valuable assistance rendered during the period of their Demonstratorship in the Siemens Laboratory, King's College, London.

12.4.97

charge and capacity. Suppose that from $t = 0$ to $t = t$, $x_t = \mathrm{X}$, and before that time $x_t = 0$, then $y_t = \mathrm{X}\int_0^t \psi(\omega)\,d\omega$, and $\frac{dy_t}{dt} = \psi(t)$; thus $\psi(t)$ is the conductivity after electrification for time t. It has of course been long known that in stating the conductivity or resistance of the di-electric of a cable, it is necessary to state the time during which it has been electrified ; hence $\psi(t)$ is for many insulators not constant. $\psi(\infty)$ may perhaps be defined to be the true conductivity of the condenser, but at all events we have $\psi(t)$ as the expression of the reciprocal of a resistance measurable, if we please, in the reciprocal of ohms. For convenience we now separate $\psi(\infty) = \beta$ from $\psi(\omega)$ and write for $\psi(\omega)$, $\psi(\omega) + \beta$. If we were asked to define the capacity of our condenser we should probably say : "suppose the condenser be charged to potential X for a considerable time and then be short-circuited, let Y be the total quantity of electricity which comes out of it, then Y/X is the capacity." If T be the time of charging $y_t = \mathrm{X}\int_0^{\mathrm{T}} \{\psi(\omega) + \beta\}\,d\omega$ at the moment of short circuiting ; $y_t = \mathrm{X}\int_t^{\mathrm{T}+t} \{\psi(\omega) + \beta\}\,d\omega$ after time t of discharge. The amount which comes out of the condenser is the difference of these, or $\mathrm{Y} = \mathrm{X}\left\{\int_0^{\mathrm{T}} \psi(\omega) + \beta\,d\omega - \int_t^{\mathrm{T}+t} \psi(\omega) + \beta\,d\omega\right\}$; if t be infinite $\psi(t) = 0$, and $\mathrm{Y} = \mathrm{X}\int_0^{\mathrm{T}} \psi(\omega)\,d\omega$; or we now have capacity expressed as an integral of $\psi(\omega)$ and measurable in microfarads, and it appears that the capacity is a function of the time of charge increasing as the time increases. Experiments have been made for testing this point in the case of light flint glass, showing that the capacity was the same for 1/20000 second and for ordinary durations of time ('Phil. Trans.,' 1881, p. 356), doubtless because $\int_{1/20000}^{\infty} \psi(\omega)\,d\omega$ is small compared with $\int_0^{1/20000} \psi(\omega)\,d\omega$. Now $\int_0^t \psi(\omega)\,d\omega$, when t is indefinitely diminished, may be zero, have a finite value, or be infinite ; in fact it has a finite value. The value of $\psi(\omega)$ when ω is extremely small can hardly be observed ; but $\int_0^t \psi(\omega)\,d\omega$, when t is small, can be observed. It is therefore convenient to treat that part of the expression separately, even though we may conceive it to be quite continuous with the other parts of the expression. $\int_0^t \psi(\omega)\,d\omega$, when t is less than the shortest time at which we can make observations of $\psi(\omega)$, is the instantaneous capacity of the condenser. Call it K and suppose the form of ψ to be so modified that for all observed times it has the observed values, but so that $\int_0^t \psi(\omega)\,d\omega = 0$, when t is small enough.

Then $y_t = \mathrm{K}x_t + \int_0^{\infty} x_{t-\omega}\{\psi(\omega) + \beta\}\,d\omega$. Here the first term represents capacity, the second residual charge, the third conductivity, separated for convenience, though really all parts of a continuous magnitude. Suppose now our condenser be submitted to a periodically varying electromotive force, that

$$x_t = \mathrm{A}\cos pt,$$

then

$$y_t = \mathrm{A}\left\{\mathrm{K}\cos pt + \int_0^\infty \cos p(t-\omega)\,[\psi(\omega)+\beta]\,d\omega\right\}$$

$$= \mathrm{A}\left\{\mathrm{K}\cos pt + \cos pt\int_0^\infty \cos p\omega\psi(\omega)\,d\omega + \sin pt\int_0^\infty \sin p\omega\psi(\omega)\,d\omega\right\}.$$

The effect of residual charge is to add to the capacity K the term $\int_0^\infty \cos p\omega\psi(\omega)\,d\omega$, whilst the term $\sin pt\int_0^\infty \sin p\omega\psi\omega\,d\omega$ will have the effect of conductivity as regards the phases of the currents into the flask. Thus the nature of the effect will depend upon the form of the function $\psi(\omega)$. An idea may be obtained by assuming a form for $\psi(\omega)$, say $\psi(\omega) = \frac{\mathrm{C}}{t^m}$, where m is a proper fraction. This is a fair approximation to the truth. Then

$$\int_0^\infty \cos p\omega\psi(\omega)\,d\omega = \Gamma(1-m)\cos(1-m)\,\pi/2/p^{1-m},$$

$$\int_0^\infty \sin p\omega\psi(\omega)\,d\omega = \Gamma(1-m)\sin(1-m)\,\pi/2/p^{1-m}.$$

If m is near to unity, capacity is almost entirely affected; otherwise the effect is divided between the two, and dissipation of energy will occur. It is interesting to consider what sort of conductivity a good insulator such as light flint glass, according to this view of capacity, residual charge, and conduction, would have at ordinary temperatures if we could measure its conductivity after very short times of electrification; if, in fact, we could extend the practice used for telegraph cables and specify that the test of insulation should be made after the one hundred millionth of a second instead of after one minute, as is usual for cables. The capacity of light flint measured with alternating currents with a frequency of two millions a second is practically the same as when measured in the ordinary way; that is, its capacity will be 6·7. Its index of refraction is 1·57 or $\mu^2 = 2{\cdot}46$, or, say, 2·5. We have then to account for 4·2 in a certain short time. The current is an alternating current, and we may assume as an approximation that it will be the residual charge which comes out in one-sixth of the period which produces this effect on the capacity; therefore $\int_0^{1/12\times 10^6}\psi(\omega)\,d\omega = \frac{4\cdot 2}{6\cdot 7}$ × capacity of the flask as ordinarily measured. The capacity of a fairly thin flask may be taken to be 1/1,000 microfarad to 2/1,000 microfarad; hence we may take $\int_0^{1/12\times 10^6}\psi(\omega)\,d\omega$ to be 10^{-9} farad; if $\psi(\omega)$ were constant during this time its value must be $12 \times 10^6 \times 10^{-9} = \frac{1}{80}$ ohms^{-1} about. The value of $\psi(\omega)$

is far from constant, and hence the apparent resistance of that extraordinarily high insulator, a flint-glass flask, must be, for very short times, but still for times enormously large compared with the period of light waves, much less than 80 ohms.

[Added 11th March, 1897.—Somewhat similar considerations are applicable to conduction by metals. MAXWELL pointed out that the transparency of gold was much greater than would be inferred from its conductivity measured in the ordinary way. To put the same thing another way—the conductivity of gold as inferred from its transparency is much less than as measured electrically with ordinary times. Or the conductivity of gold increases after the application of electromotive force. Suppose then we have a current in gold caused by an electromotive force which is increasing, the current will be less than it would be if the electromotive force were constant, by an amount approximately proportional to the rate of increase. If u be the current, ξ the electromotive force, $u = \alpha\xi - \beta\xi^{\cdot}$ where α is the conductivity as ordinarily measured. This gives us the equation of light transmission $\alpha\xi^{\cdot} - \beta\xi^{\cdot\cdot} = \frac{d^2\xi}{dx^2}$ assuming that we have no capacity in the gold.

Professor J. J. THOMSON gives as a result of some experiments by DRUDE that the capacity of all metals is negative. This conclusion is just what we should expect, if we assume, as MAXWELL has shown, that the conductivity of metals increases with the time during which the electromotive force is applied.]

The experiments herein described are addressed to ascertaining the effect of temperature, first on residual charge as ordinarily known, second on capacity as ordinarily known, third to examining more closely how determinations of capacity are affected by residual charge, fourth to tracing the way in which the properties of insulators can continuously change to those of an electrolyte as ordinarily known. The bodies principally examined are soda-lime glass, as this substance exhibits interesting properties at a low temperature, and ice, as it is known that the capacity of ice for such times as one-tenth of a second is about 80, and for times of one-millionth of a second of the order of 3 or less.

RESIDUAL CHARGE AS AFFECTED BY TEMPERATURE.

Experiments on this subject have been made by one of us which showed that residual charge in glass increases with temperature up to a certain temperature, but that the results became then uncertain owing to the conductivity of the glass increasing. These experiments were made with an electrometer, the charge set free in the flask being measured by the rate of rise of potential on insulation. We now replace the electrometer by a delicate galvanometer and measure the current directly without sensible rise of potential.

Fig. 1 gives a diagram of connections. The glass to be experimented upon is blown into a thin flask F, with thick glass in the neck to diminish the effect of charge creeping above the level of the acid, and is filled with sulphuric acid to the shoulder; it is then placed in sulphuric acid in a glass beaker, which forms the inner lining of a copper vessel consisting of two concentric tubes between which oil is placed. Thermometers, T_1 T_2, placed in the acid outside the jar and in the oil, are made to register the same, or nearly the same, temperatures when taking observations, but T_1 gives the temperature taken for the flask. The flask is heated by a Bunsen burner placed under the copper vessel. Two electrodes a, c, insulated from

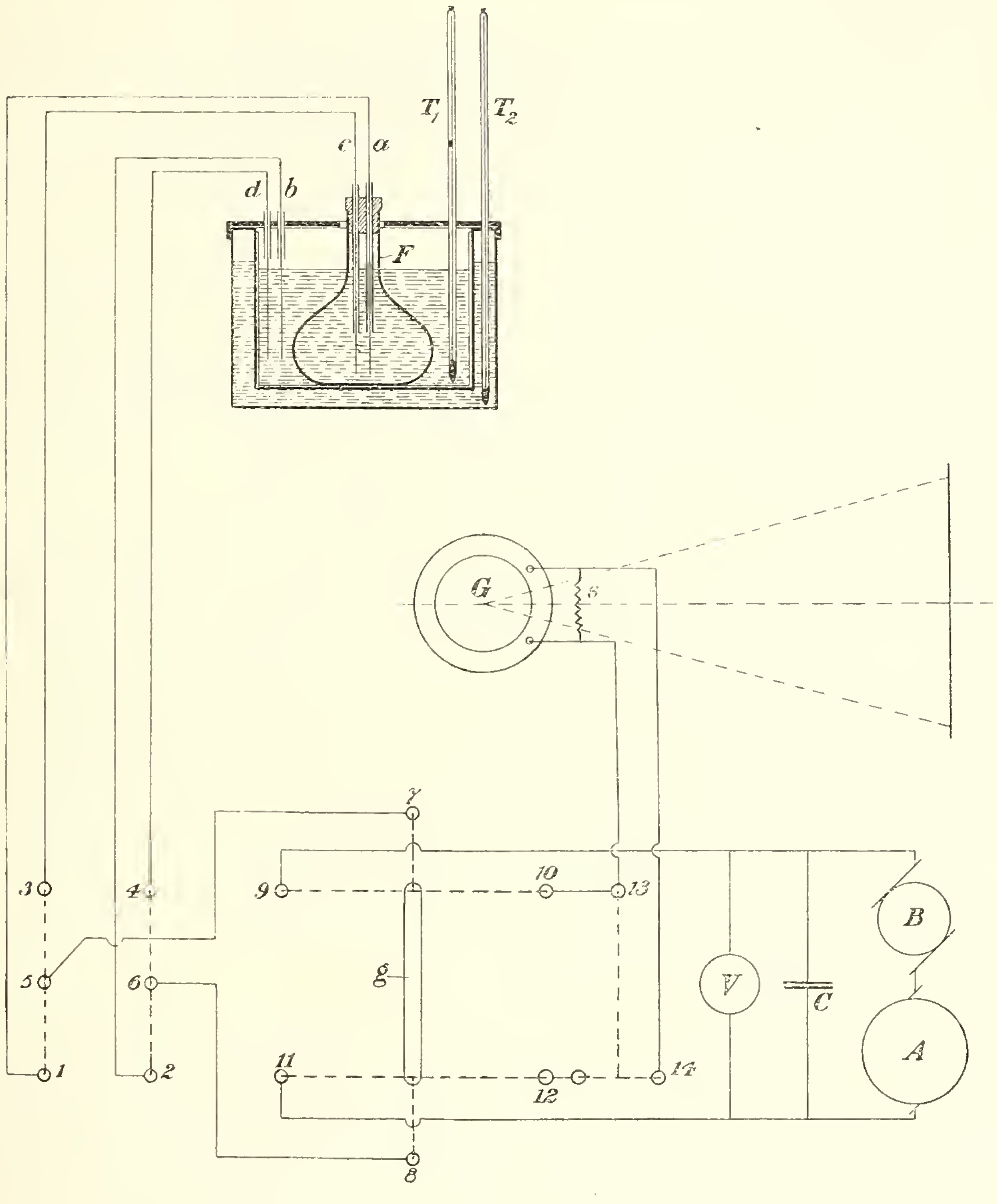

Fig 1

one another, and from the flask by means of sealing wax and glass tubes, dip into the sulphuric acid forming the inner coating of the jar, and similarly, electrodes *b*, *d* dipping into the outer acid make connection with the outer coating. The acid inside and out was made to wet the flask up to a level higher than the acid would reach at the highest temperatures.

The four electrodes, *a*, *b*, *c*, *d*, are connected respectively by thin copper wires, with four mercury cups 1, 2, 3, 4, cut in a block of paraffin, and, by means of a reversing switch *a*, *b* and *c*, *d*, can be connected respectively to mercury cups 5, 6. Cups 5, 6 are connected respectively to 7, 8 by thin wires, which can in turn be connected with or disconnected from the source of charge 9, 11.

The steady potential difference of about 1,500 volts is obtained from a Siemens alternator A, in series with a revolving contact maker B fixed to the alternator shaft and making contact once per complete period, there being six periods per revolution. The contact-maker is set to make contact when the potential difference is a maximum. A condenser C, and a Kelvin vertical electrostatic voltmeter V, are placed in parallel between the connecting wires leading to mercury cups 9, 11.

The galvanometer G has a resistance of 8,000 ohms and is inclosed in an iron box which acts as a magnetic shield. The box is supplied with a small window for the ray of light to pass through it from an incandescent lamp to the mirror from which it is reflected back through the window to a scale at a distance of 12 feet from the mirror. The divisions on this scale are $\frac{1}{10}$th of an inch apart, and an average sensibility for this instrument is $\cdot 3 \times 10^{-9}$ ampere per division of the scale. The galvanometer is supplied with a shunt S, and has its terminals connected to mercury cups 13, 14 on the paraffin block. These mercury cups are connected to cups 10, 12 respectively, which can at will be connected to 7, 8, by one motion of the glass distance-piece *g* forming part of the reversing switch which places 9, 11, or 10, 12, in contact with 7, 8. A switch is so arranged that 13, 14 can be connected at will, that is, the galvanometer is short circuited.

The process of charging, discharging, and observing, is as follows:—Near the observer is a clock beating seconds which can be distinctly heard by the observer. Initially, the cups 9, 11, are disconnected from 7, 8; but 5, 1, and 6, 2, are connected. At the given moment the reversing switch is put over connecting 7, 9, and 11, 8; the jar is then being charged through electrodes *a*, *b*. This goes on for the desired time, during which charging volts and zero of the instrument are noted. At the end of the time required for charge, the main reversing switch is put over connecting 7, 10, and 8, 12; next the subsidiary switch is put over connecting 3 to 5 and 4 to 6, and on opening the short-circuiting switch, the spot of light is deflected and allowed to take up its natural state of movement determined by residual charge, readings being taken at stated epochs after discharge is started. This whole operation, including an adjustment of the shunt when necessary, was so speedily accomplished that reliable readings could be taken 5 seconds after discharge is started. By using two electrodes, polarization of electrodes is avoided, and the gradually-diminishing current through the galvanometer is that due to residual charge. The conductivity of the jar is determined by removing the glass distance-piece g, connecting 7 to 9, 8 to 12, and 10 to 11, and noting the steady deflection on the galvanometer for a given charging potential difference.

In the ice experiment, the conductors from 3, 4, are used both for charging and discharging. The form of condenser used when dealing with ice and liquid dielectrics is shown in fig. 2. It consists of seven platinum plates, a, b, c, d, e, f, g, each measuring 2 inches by 3 inches, and of a thickness ·2 millim., separated from each other by a distance of 2·7 millims. To each plate are gold-soldered four platinum wires—two top and two bottom. Plates a, c, e, g, form the outer coating of the condenser, and are kept in their relative positions by cross connecting wires h, gold-soldered to the wires at each end of each plate. Similarly, plates b, d, f, which form the other and inner coating of the condenser, are fixed relatively to one another by cross connecting wires i. The relative positions of the two sets of plates are fixed by glass rods 1, 2. The terminals of the condenser are, for the inner plates the prolonged wire 3, and for the outer plates the wires 4, 4. These are bent round glass rods 5, 6, which resting on the top of a beaker support the plates in the fluid. The glass tubes on the wires 3, 4, 4, are for the purpose of securing good surface insulation. The glass beaker is conical, so as to remain unbroken when freezing the distilled water within. This was accomplished

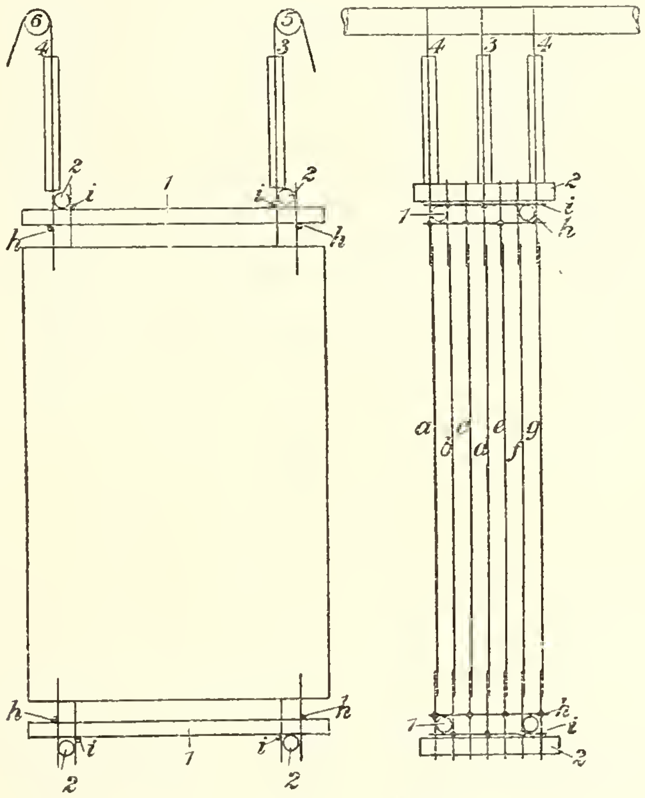

Fig 2.

by surrounding the beaker with a freezing mixture of ice and salt, the lower temperature being obtained by further cooling in carbonic acid snow.

The same blue flask, which was the subject of the earlier experiments, was mounted as shown in fig. 1, and the residual charge observed for various temperatures. This glass is composed of silica soda and lime; the colour is due to oxide of cobalt in small quantity.

Out of a large number of experiments the data in Tables I. and II. give the general character of the results.

TABLE I.

Time in seconds.	15° C.	$34\frac{1}{2}$.	$54\frac{1}{2}$.	70.	85.	117.	132.	Remarks.
10	246	..	..	..	..	9770	7256	Blue flask. 6th and 7th November, 1894. Sensibility of galvanometer, $\cdot 378 \times 10^{-9}$. Duration of charge, 2 minutes. Charging volts, 1250
15	..	376	1176	2785	5445	..	..	
20	121	265	1030	2586	4100	3590	3010	
30	87	209	892	2070	2980	2150	1735	
60	46	131	683	1320	1510	950	778	
120	$22\frac{1}{2}$	91	483	720	688	440	350	
300	$9\frac{1}{4}$	62	256	260	210	164	107	
600	..	..	123	110	..	86	less than 59	

TABLE II.

Time in seconds.	14° C.	55.	70.	110.	137.	Remarks.
10	205	..	..	11740	12400	Blue flask. 13th November, 1894. Sensibility of galvanometer, $\cdot 407 \times 10^{-9}$. Duration of charge, 2 minutes. Charging volts, 1250.
20	99	1230	2850	4790	4340	
60	38	837	1560	1212	990	
120	17	594	878	487	366	
300	5	308	314	134	..	

TABLE III.

3rd January, 1895.				4 January, 1895.			Remarks.
Time in seconds.	8° C. 5 min. charge.	117 1 min.	$117\frac{1}{2}$ 1 min.	8° C. 5 min. charge.	122 1 min.	$122\frac{1}{2}$ 1 min.	
10	75	..	258	70	..	1100	New window glass flask. Sensibility of galvanometer, $\cdot 358 \times 10^{-9}$. Resistance of flask, 8° C., 3340×10^{6} ohms. Charging volts, 1500.
20	43	123	148	44	..	664	
30	30	105	109	32	400	..	
60	18	80	73	19	240	240	
180	$7\frac{1}{2}$	..	56	$7\frac{3}{4}$	69	68	

The figures given are the deflections of the galvanometer in scale divisions corrected for the shunt used. Recalling that one scale division means a known value in amperes, that a known potential in volts is used, these figures can readily be reduced to ohms $^{-1}$. The capacity of the flask is 0·0026 microfarad at ordinary temperatures and times, and the specific inductive capacity of its material under similar conditions is about 8. Hence one could reduce to absolute conductivities of the material. It is more interesting to consider how fast the capacity is changing. Take the first result given in Table III. for another flask 75 at 10 seconds; this means a conductivity $75 \times 0{\cdot}358 \times 10^{-9}/1{,}500 =$ about $0{\cdot}179 \times 10^{-10}$, and this is, of course, the rate in farads per second at which the capacity is changing in that experiment compared with a capacity of the flask $\frac{1}{2}10^{-3}$ microfarad measured with the shortest times, or, to put it shortly, the flask owing to residual charge is changing capacity at the rate of about 3 per cent. per second. These figures also show that the residual charge up to 20 seconds increases greatly with the temperature; the residual at 60 seconds rises with the temperature up to about 70° C. or 80° C., and then diminishes; residual charge at 300 seconds begins to diminish at about 60° C. One may further note the way in which the form of the function $\psi(\omega)$ changes as temperature rises. Compare in Table I. the values for 20 and 30 seconds, the ratios are :—

Temperature . . .	15	34½	54½	70	85	117	132,
Ratio	1·39	1·27	1·16	1·25	1·38	1·67	1·74.

In other words, if we expressed $\psi(\omega)$ in the form C/t^m, we should find m first diminishes as temperature rises to 54°, then increases as the temperature further rises. This has an important bearing upon the effect of residual charge on apparent capacity and resistance.

It will be noticed that the residual charge, for the same time, at high temperatures, is somewhat greater in Table II. than I. The results in Table I. were obtained on November 7th, 1894; those in Table II. on November 13th, 1894. There is no doubt but that heating this glass and submitting it to charge when heated, alters the character of the results in such manner as to increase residual charge for high temperatures. To test this more thoroughly, a new flask was blown out of window glass composed of silica lime and soda without colouring matter, and on January 3rd, 1895, was charged and discharged in the ordinary manner. After the results given in Table III. for January 3rd were obtained, the flask was charged for 21 minutes at 1,500 volts, the direction of charge being reversed after 10 minutes, the temperature of the flask being 133°. We see that on January 4th, Table III., the same effect is observed, namely an apparent increase in residual charge for the same time at high temperatures. This may probably be attributed to a change in the composition of the material by electrolysis.

Capacity.

(a.) *Low Frequency.*

Fig. 3 gives a diagram of connections, showing how the apparatus is arranged for the purpose of determining the capacity of poor insulators, such as window glass or ice, at varying temperatures. This is a bridge method, the flask F being placed in series with a condenser of known capacity K, and on the other side non-inductive resistances R_1, R_2. By means of keys k_1, k_2, the bridge can be connected to the poles of a Siemens alternator A; its potential difference is measured on a Kelvin multicellular voltmeter V. On the shaft of the alternator is fixed the revolving contact-maker B, which makes contact once in a period, and the epoch can be chosen.

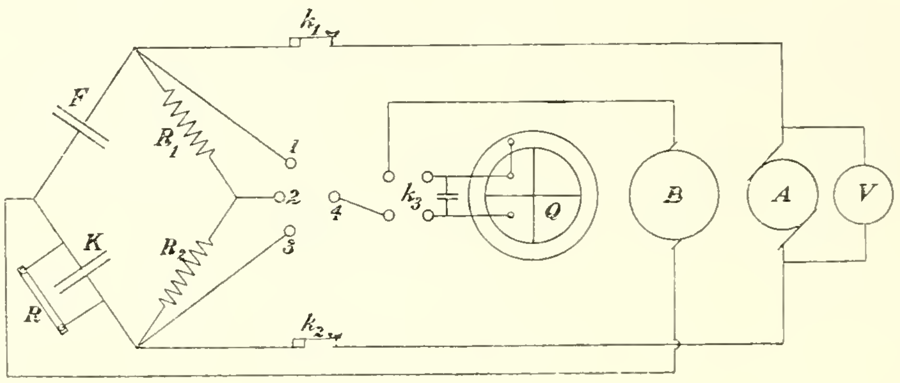

Fig 3.

The Kelvin quadrant electrometer Q has one pair of quadrants connected to a pole of the revolving contact-maker B, and the other to a mercury cup 4 in a block of paraffin. The other terminal of B is connected to the junction between F and K; by means of mercury cups 1, 2, 3, the electrometer can be connected through the contact-maker to either end, or to the middle of the bridge.

The compensating resistance R is the resistance due to pencil lines drawn on fine obscured glass strip,* about 12 inches long and $\frac{3}{4}$ inch wide, contact being made at each end by means of mercury in a small paraffin cup, and the whole varnished whilst hot with shellac varnish. A series of these resistances was made, ranging in value from a few megohms to a few tens of thousands of ohms. For the purpose of these experiments a knowledge of their actual resistance is of no moment, although for the purpose of manipulation their resistances are known.

The method of experiment is as follows :—Mercury cups 1 and 4 are connected by a wire, placing the electrometer and contact-maker across F, and the contact-maker is moved until it indicates no potential. Cups 3, 4 are now connected, and resistance R is adjusted until the electrometer again reads zero. After a few trials, alternately placing the bridge between 1, 4 and 3, 4, and adjusting R, the potentials are brought into the same phase, that is, the potential across the electrometer is zero in each case for the same position of the contact-maker. Mercury cups 2, 4 are now connected, the contact-maker B is adjusted to the point of maximum potential, and R_1, R_2 adjusted until balance is obtained. We now know that $K/F = R_1/R_2$.

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* See 'Phil. Mag.,' March, 1879

k_3 is the ordinary key supplied with the electrometer, which reverses the charge on the quadrants or short circuits them. The range of frequency varies from 100 to 7 or 8 complete periods per second.

(B.) *High Frequency.*

For high frequencies a method of resonance is used,* and the apparatus shown in fig. 4. The primary coil consists of 1, 9, or 160 turns of copper wire 4 feet in diameter, having a condenser K_1 in its circuit and two adjustable sparking knobs *a*, *b*. The secondary is placed with its plane parallel to that of the primary, and usually at a distance of 4 or 5 feet from it; adjustable spark knobs *c*, *d* are provided in its circuit, which consists of 1, 9, or 160 turns of copper wire of the same diameter as the primary. The diameter of the wires for the 1, 9, and 160 turns are respectively 5·3, 2·65, and 1·25 millims. A Ruhmkorff coil excites the primary. Between the spark knobs *c*, *d* are placed the capacity to be found F, and a large slide condenser K. The method is one of substitution, that is to say, maximum resonance is obtained with both condensers attached by variation of K; F is removed and maximum resonance again obtained by increase of K. In order to bring K on the scale for the two maxima, it is necessary to adjust K_1, the condenser in the primary. This condenser consists of a

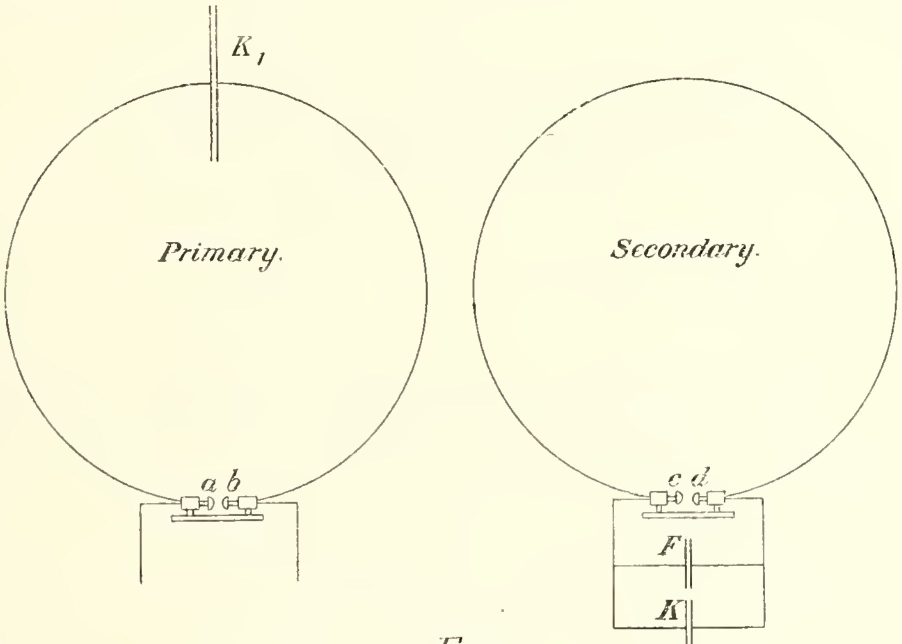

Fig 4.

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* This method, we find, has been used by THWING, 'Physical Society's Abstracts,' vol. 1, p. 79.

sheet of ebonite with tin-foil on either side; three such condensers are available, and by variation of the area of tin-foil, if necessary, a suitable value for K_1 was speedily obtained. Platinum-foil was used for the electrodes in the acid inside and outside the jar in the glass experiments instead of wire, as shown in fig. 1, in order to secure that the connections should not add materially to the self-induction of the circuit.

The frequency is calculated from the formula

$$\text{Frequency} = \frac{1}{2\pi\sqrt{\text{K L } 10^{-15}}}$$

where

K is the capacity in secondary in microfarads,
L is the self-induction in centimetres.

$$\text{L} = 4\pi n^2 a \left(\log_\epsilon \frac{8a}{r} - 2\right)$$

where

n is the number of turns on the secondary,
$2a$ is the diameter of the ring = 4 feet,
$2r$ is the diameter of wire on secondary.

When $n = 1$, $\text{L} = 4230$ centimetres. If K be taken ·00096 microfarad the frequency is $2{\cdot}5 \times 10^6$.

The lowest frequency we have tried with this apparatus is when $n = 160$ $\text{L} = 136 \times 10^6$. If K be taken ·0028 microfarad, the frequency is 8,400.

That the capacity of some kinds of glass does not vary much with a moderate variation of temperature is known ('Phil. Trans.,' 1881, p. 365). Experiments were tried on the same blue flask as before, using the method in fig. 3. The results obtained and many times repeated for a frequency of 70 or 80 are given in Table IV. As the specific inductive capacity of this flask, measured in the ordinary manner, is about 8, it appears that at 170° it is about 21. Knowing from the results in Tables I. and II. how great was the residual charge for high temperatures and short times, it appeared probable that the result would depend upon the frequency. This was found to be the case, as shown by the results of November 26, 1894, Table IV., the apparent capacity being somewhat more than one-half at frequency 100 of what it is at frequency 7·3. Experiments on the window-glass flask show the same result.

The next step was to determine whether or not this large increase of apparent capacity was due to residual charge. To do this the resonance experiments fig. 4 were resorted to and the capacity of the flask was determined with a frequency of about 2×10^6; it was found to be sensibly the same whether the flask were hot or cold. The results show that the capacity varies from 185 to 198 in arbitrary units with a variation of temperature from $25\frac{1}{4}$° to 127°. With frequency 8,400 the capacity varies from 240 to 285 in arbitrary units for a variation of temperature from 21° to 122°, but here the sensibility was not so good as with the higher frequency. We conclude that the apparently great capacity of this glass at a temperature from 120° to 170° is due to residual charge, but that the effects of this part of the residual charge are not greatly felt if the frequency is greater than about 10,000 a second.

The extent to which the capacity of the window-glass flask is affected by the frequency at ordinary temperatures, 8° C., is shown by the following figures :—

Frequency	12	39	70
Capacity	·00075	·0008	·001

Table IV.

20th November, 1894. Frequency, 72 ; volts, 70.		21st November, 1894. Frequency, 85½ ; volts, 71½.		26th November, 1894. Temperature, 120° C.		
Temperature. C.	Capacity of flask in terms of itself at 15°.	Temperature. C.	Capacity of flask in terms of itself at 25° C.	Frequency.	R_2/R_1.	Remarks.
15	1	25½	1	7·3	1·27	Standard condenser unaltered throughout experiment
92	1·31	54	1·05	12	1·11	
117	1·66	95	1·27	39½	·87	
154	2·6	120	1·59	71½	·78	
		170	2·61	100	·75	

Conductivity after Electrification for Short Times.

The Battery.—This consists of 12 series of small storage cells, fig. 5, each series containing 50 cells. The poles of each set of 50 cells are connected to mercury cups in a paraffin block, and numbered 1, 3, 5, . . . 21, 23, on the positive side; 2, 4, 6, . . . 22, 24, on the negative. Cups *b*, *d*, are connected to the poles of the 56 cells in the Laboratory, and therefore, by connecting *d*, 1, 2 . . . 21, 23, together on the one side, and 2, 4, . . . 22, 24, *b*, together on the other side, the cells can be charged in parallel. For the purpose of these experiments, a large potential difference is required; this is obtained by removing the charging bars, and replacing them by a series of conductors connecting x to 1, 2 to 3 . . . 22 to 23, 24 to y. In this manner, the whole of the 600 cells are placed in series with one another. Across the terminals x, y, are placed a condenser K_3 of about 4·3 microfarads, and a Kelvin vertical electrostatic voltmeter V. In order to change over quickly, and for the purpose of safety, the charging bars and connections for placing the cells in series are mounted on wood.

The Contact Apparatus.—This consists of a wooden pendulum carrying lead weights w_1, w_2, which were not moved during the experiments. The pendulum is released from the position p by the withdrawal of a brass plate, and, swinging forward, strikes a small steel contact piece f, carried on a pivoted arm of ebonite. The initial position of this ebonite arm is determined by a contact pin e, about $\cdot\frac{1}{16}$ inch diameter, contact being maintained by a spring m with an abutting rod insulated from a brass supporting tube by means of gutta-percha. This insulated rod is continued by a copper wire to the insulated pole of a quadrant electrometer Q. The brass supporting tube is continued by means of a metallic tape covering on the outside of the insulated wire, and is connected to the case and other quadrant of the electrometer. If, then, the pendulum be released from position p, the time which elapses between the terminal piece g first touching the plate f, and the time at which contact is broken between e and the insulated stop is the shortest time we have been able to employ in these experiments, its duration being ·00002 second.

For longer times an additional device, shown in plan only, is used. It consists of a brass pillar h, which carries a steel spring S, and which is moved to and fro in V-shaped slides by means of a screw provided with a milled head n, which is divided into twenty equal parts on the outside surface. A pointer fixed to the frame indicates the position of the head, and a scale on the brass slide shows the number of revolutions of the head from zero position. The pendulum steel piece g is of sufficient width to touch the spring S as it moves forward and strikes the plate f. The zero of the spring S is determined electrically by moving forward the pillar h, and noting the position of the milled head when contact is first made, the steel piece g being in contact with f, but not disturbing its initial position. The plate f is connected by a flexible wire with the slides which are in connection with the spring S through its support h. When, therefore, the spring S leads the plate f by any distance, the time of contact is that time which elapses between g first striking S and the severance of contact between the pin e and its stop, always supposing that g keeps in contact with S. A good deal of trouble was experienced before making this contact device satisfactory. The ebonite arm carrying e and f was originally of metal, f being insulated; but inductive action rendered the results untrustworthy. Then again, the spring S, when first struck by the pendulum evidently again severed contact before f was reached. To get over this difficulty a subsidiary series of fine steel wires were attached to S, so that as the pendulum moves forward the wires are one after the other struck. In order that the pendulum should not foul these wires or the spring S on its return to position p, it was slightly pressed forward by the hand at its central position.

The method adopted is that of the bridge. Starting from mercury cups x, we proceed by a fine wire to the terminal i, and thence, by a wire passing down the pendulum, to g. From g we pass through spring S and the piece f during contact to one end of the bridge. The flask F, or condenser to be experimented upon, is placed in series with metallic resistances *a*, these forming one arm of the bridge, the condensers K_1, K_2 forming the other arm. The stop *e* is connected to the junction between *a* and F; and the junction of K_1, K_2 is connected to the

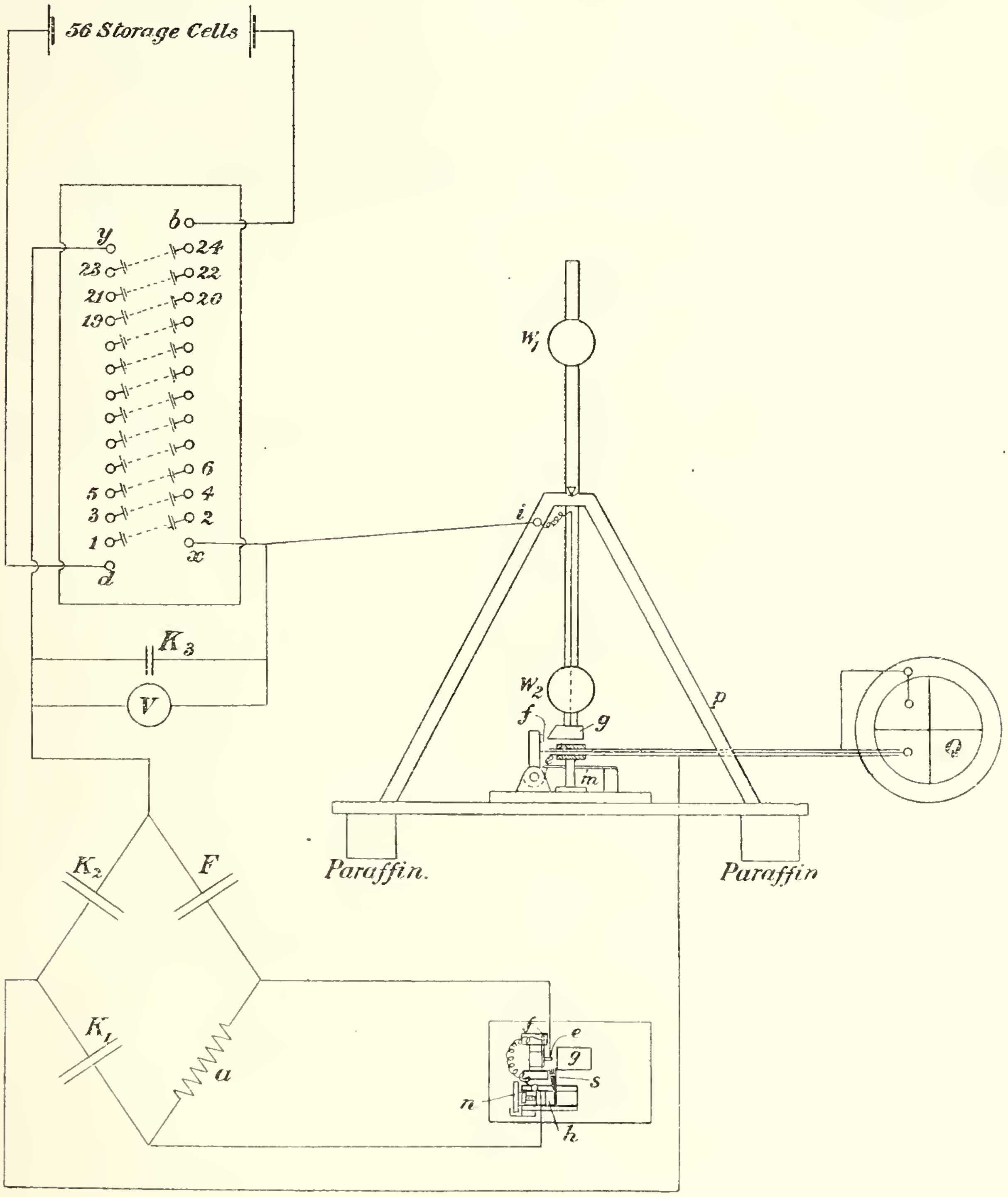


Fig 5

case of the electrometer by the outer conductor of the insulated wire leading to the instrument. The whole of the pendulum arrangement is supported on paraffin feet.

In the first instance pencil lines on glass were used for *a*, and K_1, K_2; but, for short times and varying current densities it was proved that these were unreliable, when a knowledge of their actual resistance at the time of contact is taken to be the same as measured in the ordinary way on a Wheatstone bridge.

Time of Contact.—The connections were altered from those in fig. 5 to those in fig. 6. Eight dry cells having low internal resistance were used for charging. In fig. 6 let K be the capacity of the condenser, equal to $\frac{1}{3}$ microfarad. Let k be the capacity of the quadrant electrometer at rest in zero position, equal to ·000015 microfarad. Let R be the insulation resistance of K, and r the resistance through which the condensers are charged. Let E be the E.M.F. of the battery, V be the E.M.F. of condenser, and t the time of contact in seconds.

Then

$$(K + k)\dot{V} + \frac{V}{R} = \frac{1}{r}(E - V)$$

$$V = \frac{RE}{R + r}\left(1 - \epsilon^{-t\frac{R + r}{Rr}\cdot\frac{1}{K + k}}\right).$$

To determine E. Let $R = \infty$, $K = 0$, $r = 0$; the deflection of the electrometer needle from zero after the pendulum has struck gives E in scale divisions.

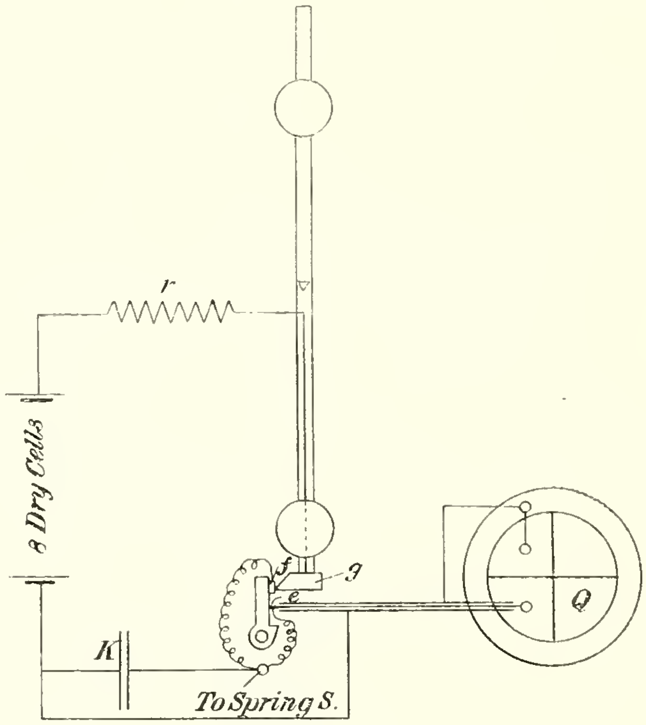


Fig 6.

To determine t. Let K be known and great as compared with k. Let $R = \infty$, and let r be such that the steady deflection from zero, V, after pendulum has struck, is about equal to half E.

$$V = E\left(1 - \epsilon^{-\frac{t}{Kr}}\right),$$

which gives

$$t = rK \log_\epsilon \frac{E}{E - V}.$$

The following are the values of t in seconds, so deduced, in terms of revolutions of the milled head n from zero :—

Turns of milled head from zero.	0	$\frac{1}{2}$	1	2	3	4	5	6
Time of contact in seconds.	·00002	·00035	·00099	·0028	·006	·009	·011	·014

The experiments have so far dealt with frequencies ranging from 2×10^6 to 8,000, and 100 to 10. The gap between 8,000 and 100, during which the great effects of residual charge become apparent, is filled up by experiments with the pendulum apparatus just described. An attempt was made to fill up this gap by means of the method shown in fig. 6, from which the effect on the capacity could be found for various times of contact, but this method was finally abandoned and used only for the determination of times of contact.

Referring to fig. 5, F is the same window-glass flask mentioned above, and mounted as in fig. 1 ; a is a non-inductive metal resistance, the effect of the capacity of which was at the most, when a is large, only capable of disturbing our experiments to the extent of eight per cent., but in most cases the disturbance is a small fraction of this ; K_1 is a one-third microfarad condenser, and K_2 the large slide condenser used in the other experiments. The advantage of this method of experiment is that the charging potential difference V is great, and the actual ohmic resistance of a is small as compared with that of the flask F. In this manner the effect of the instantaneous capacity of the flask is overcome at once and the after effects due only to residual charge can be examined directly. The results are shown in Table V.

TABLE V.—Window-Glass Flask. 16th–31st October, 1896.

a. Resistance box.

K_1. $\frac{1}{3}$rd *m.f.* = 118,000 divisions of large slide condenser.

K_2. Large slide. When at zero = 100 of its own scale divisions.

„ „ When at 435 = ·00146 *m.f.*

K = ·0005 *m.f.* from highest frequency resonance experiments.

In the diagram, fig. 7, giving curves of conductivity and time for given temperature,

1 centim. vertical = 2×10^{-8} $(l^{-1}t)$.

1 centim. horizontal = 2×10^{-4} (t) seconds.

Therefore, area $\times\ 4 \times 10^{-6}$ gives capacity in microfarads.

Time of contact.		Temperature of Flask, 15·4° C.								
Turns of milled head.	Time in seconds.	Large slide position K_2	a in 10^6 ohms.	$\epsilon^{-\frac{t}{a\mathrm{K}}} = \mathrm{A}$.	Resistance of Flask c in 10^6 ohms.		$\frac{1}{c}$ in 10^{-6} $(l^{-1}t)$.	$\int \frac{1}{c}\,dt - \frac{1}{c_\infty}\,t$.		F = K + $\int \frac{1}{c}\,dt - \frac{1}{c_\infty}t$ in *m.f.*
					From $\frac{a + \mathrm{A}c}{a + c}$.	From $a\,\frac{\mathrm{K}_1}{\mathrm{K}_2}$.		Area in square centims.	*m.f.*	
0	·00002	160	·0056	·000794	3·99	2·5	·286			
0	·00002	430	·0090	·00117	2·80	2·0				
·5	·00035	..	..	..	..	..	..	11·0	·000044	·000544
1·0	·00099	160	·105	..	48	48	·0208	16·25	·000065	·000565
1·0	·00099									
2·0	·0028	70	·130	..	90	90	·0111	22·05	·000088	·000588
3·0	·0060									
	∞					1000 rough	·001			
		54–57·3° C.								
0	·00002	160	·00608	·00139	7·45	2·76	·200			
0	·00002	430	·0094	·00142	3·27	2·10				
·5	·00035	430	·055	1/330000	12·2	12·2	·085	10·7	·000043	·000543
·5	·00035	160	·025	$1/1{\cdot}6 \times 10^{12}$	11·4	11·4				
1·0	·00099	160	·065	..	29·5	29·5	·035	18·6	·000074	·000574
1·0	·00099	160	·062	..	28·1	28·1				
2·0	·0028	70	·075	..	52	52	·019	26·2	·0001	·0006
3·0	·0060									
	∞					170	·0059			

Table V.—Window-Glass Flask. 16th–31st October, 1896—(continued).

Time of contact.		Temperature of Flask, 80° C.								
Turns of milled head.	Time in seconds.	Large slide position K_2.	a in 10^6 ohms.	$e^{-\frac{t}{aK}} = A$.	Resistance of Flask c in 10^6 ohms.		$\frac{1}{c}$ in 10^{-6} $(l^{-1}t)$.	$\int \frac{1}{c}\,dt - \frac{1}{c_\infty}\,t$.		$F = K + \int \frac{1}{c}\,dt - \frac{1}{c_\infty}\,t$ in $m.f.$
					From $\frac{a + Ac}{a + c}$.	From $a\,\frac{K_1}{K_2}$.		Area in square centims.	$m.f.$	
0	·00002	160	·0041	·000058	2·52	1·86	·435			
0	·00002	430	·0079	·0063	2·04	1·80				
·5	·00035	430	·023	$1/16 \times 10^{12}$	5·1	5·1	·196	23·3	·000093	·000593
1·0	·00099	430	·066	..	14·7	14·7	·068	38·25	·000153	·000653
2·0	·0028	430	·100	..	22·3	22·3	·045	54·1	·000216	·000716
3·0	·0060	160	·065	..	29·5	29·5	·034	76·3	·000381	·000881
	∞					65	·0154			
		110–112° C.								
0	·00002	430	·0047	·00020	1·88	1·05	·714			
0	·00002	430	·0043	·000091	·973	·96				
·5	·00035	430	·0177	$1/16 \times 10^{16}$	3·9	3·9	·256	24·5	·000098	·000598
1·0	·00099	430	·020	..	4·5	4·5	·222	44·1	·000176	·000676
2·0	·0028	430	·025	..	5·6	5·6	·178	78·7	·000315	·000815
3·0	·0060	430	·029	..	6·5	6·5	·154	113·6	·000568	·00107
	∞					8·5	·118			

Window-Glass Flask. 2nd November, 1896.

Time of contact.		Temperature of Flask, 126° C.								
0	·00002	430	·0035	1/89000	·779	·780	1·28			
·5	·00035	430	·0082	..	1·83	1·83	·546	32·7	·000131	·000631
1	·00099	430	·0105	..	2·34	2·34	·427	55·5	·000222	·000722
2	·0028	430	·012	.	2·68	2·68	·373	70·8	·000283	·000783
3	·0060	430	·0133	..	2·97	2·97	·337	102·2	·000511	·000101
4	·009	430	·0135	..	3·0	3·0	·333	103	·000515	·00101
5	·011	430	·0135	..	3·0	3·0	·333	103	·000515	·00101
	∞					3·00	·333			
		145° C.								
0	·00002	430	·0018	$1/4{\cdot}36 \times 10^9$	·401	·401	2·49			
·5	·00035	430	·0032	..	·713	·713	1·40	50·8	·000255	·00075
1	·00099	430	·004	..	·892	·892	1·12	83	·00033	·00083
2	·0028	430	·0043	..	·959	·959	1·04	93	·00037	·00087
3	·0060	430	·0043	..	·959	·959	1·04	93	·00037	·00087
4	·009									
5	·011									

Table V. (continued).—10th November, 1896.

Window-Glass Flask. Solder used instead of Acid.

Time of contact.	a in ohms.	Resistance of flask c in 10^6 ohms.	Temperature of flask °C.	$\frac{1}{c}$ in 10^{-6} ohms^{-1}.
·00002	·7	·000156	about 350	6410
·00099	1·5	·000334	„ 350	3000
·0028	1·5	·000334	„ 350	3000
·011	1·5	·000334	„ 350	3000
·00002	18	·00446	285	224·0
·00002	130	·0290	229	34·5
·00002	200	·0446	219	22·4
·00002	270	·0602	203	16·6
·00099	330	·0736	202	13·6
·006	370	·0825	200	12·1
·014	370	·0825	200	12·1
Summary of results with acid.				
·00002	1000	·223	160	4·48
·00002	1800	·400	143	2·5
·00002	4700	1·05	112	·71
·00002	4100	1·86	80	·43
·00002	6080	2·76	55	·2
·00002	5600	3·99	15	·28

Let K_1, K_2, and F be discharged and let the potential difference V be applied to the bridge for time t. Let c be the ohmic resistance of the flask at the end of time t. Let K be its instantaneous capacity which is found by resonance at frequency 2×10^6. Let v be the potential across a. Then

$$\frac{v}{a} = \frac{V - v}{c} + (V - v)\cdot$$

$$v = \frac{Va}{a + c}\left\{1 + \frac{c}{a}\,\epsilon^{-\frac{a+c}{acK}t}\right\}.$$

We know a, K, and t, and measure $\frac{a}{a + c}\left\{1 + \frac{c}{a}\,\epsilon^{-\frac{a+c}{acK}t}\right\}$.

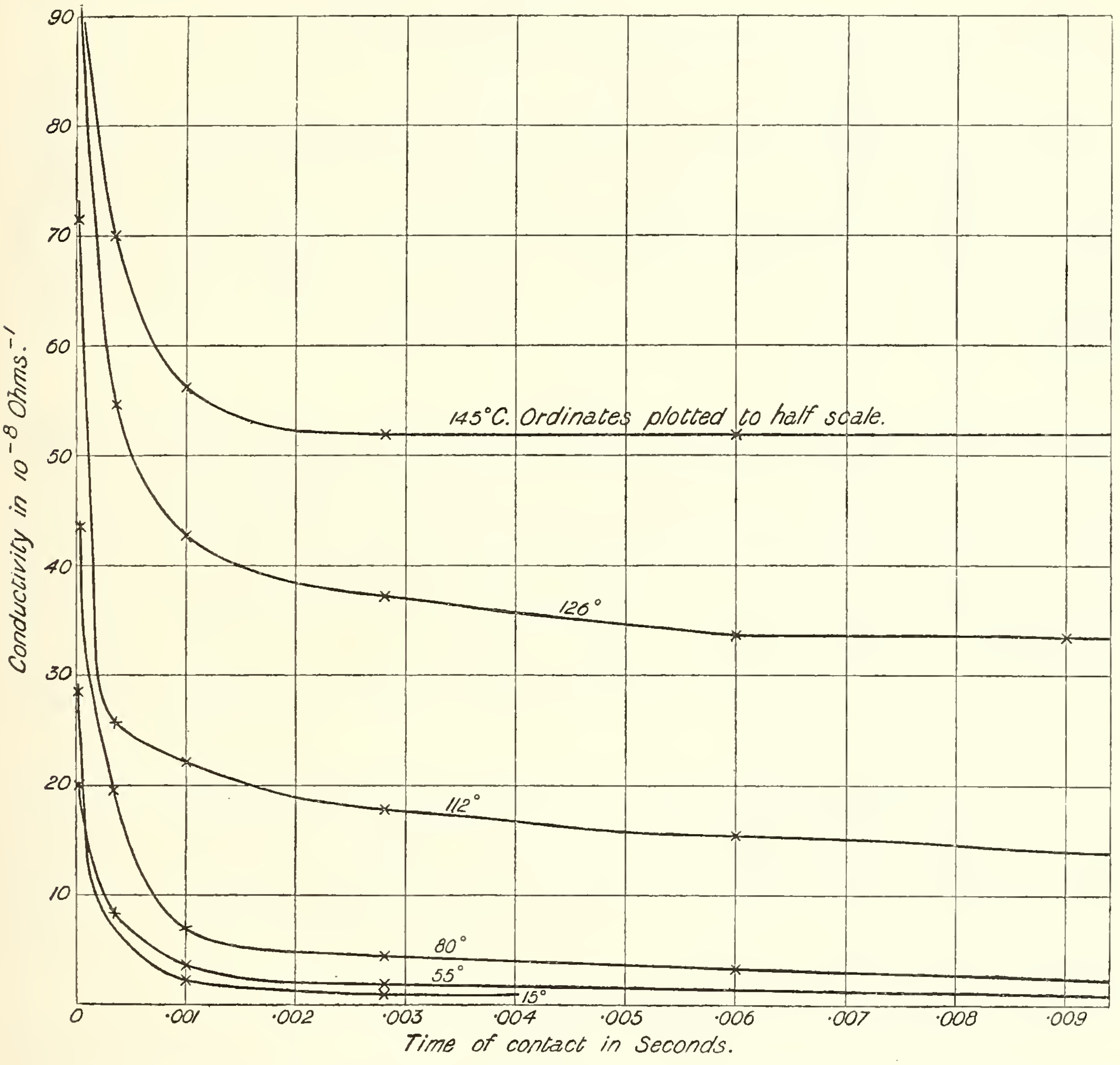
Now c is large compared to a, hence $\frac{a + c}{ac} = \frac{1}{a}$, therefore $\epsilon^{-\frac{a+c}{acK}t}$ is known; let it equal A. Then we have

$$\frac{a + Ac}{a + c} = \frac{K_2}{K_1 + K_2}.$$

We have reduced a consistent with fair sensibility until the correction due to instantaneous capacity is so small as to be almost negligible, that is, until $\frac{a + Ac}{a + c}$ is sensibly equal to $\frac{K_1}{K_2 + K_1}$.

How far we have been able to carry this can be seen by an inspection of Table V. It is only for the shortest time of contact that the correction for $\epsilon^{-\frac{t}{aK}}$ becomes at all sensible.

Fig. 7.



All temperatures from 15° to 145° were obtained by heating the flask as mounted in fig. 1; for 200° to about 350° acid was taken away and a solder, melting at about 180° C., substituted. Since the solder only half filled the flask the conductivity should be about doubled for 200° to 350° when comparing with the lower temperatures.

Since $\frac{1}{c_t}$ is the conductivity of the jar at time t, let curves of conductivities be drawn in terms of times of contact in seconds. Fig. 7 gives these curves, which have been plotted from Table V. They show that, after a given time of contact, the effect of residual charge gradually diminishes as the temperature increases, until only the conductivity of the jar for infinite times is experienced. For instance, at about a temperature of 250° the table shows that the whole effect of residual charge has died away after 1/10,000 of a second. The total capacity of the jar at time t will be $K + \int_0^t \frac{1}{c} dt - \frac{1}{c\infty} t$; where K is the instantaneous capacity which has been found by resonance to be = ·0005 microfarad for frequency 2×10^6.

$K_1 = 118{,}000$ divisions of the large slide condenser.

The curves in fig. 7 have been integrated, and their area up to ·0028 second, when reduced to microfarads and added to K, shows that, for time of contact ·0028 second, the total capacity, which is ·000588 at temperature 15·4°, is ·00087 at temperature 145°. This total capacity diminishes as the times of contact diminish, until we get to the results which resonance has shown; and then the capacity of this flask is sensibly the same for all temperatures when the frequency is of the order 2×10^6 per second.

ICE.

Ice was next examined, both in regard to its residual charge and its capacity. The residual charge is considerable, and increases as the temperature rises. Table VI. gives the residual charge of ice at two temperatures: the higher is produced by a freezing mixture of ice and salt, and is about − 18° C.; the lower by placing carbonic acid snow round the beaker, the whole being wrapped in thick felt. The apparent capacity depends on the frequency, as shown by the results in Table VII. At − 18° the capacity is twice as great with frequency 10 as with 77·6. At the lower temperature the capacity is greater for frequency 9 than for frequency 77·6, in the ratio 1·39 to unity.

The specific inductive capacity of ice was next determined, with a high frequency, by resonance: it was found to be about 3.* Decreasing the frequency to about 10,000 rendered the method by resonance less sensitive, but it is certain that the specific inductive capacity is, for this frequency, of the order 3 rather than 50. We conclude that the great deviation of ice from MAXWELL's law is due to residual charge, which comes out between frequencies 10,000 and 100.

Our next step was to determine the resistance c, as in the case of glass, by the method shown in fig. 5. The platinum plates, fig. 2, were used, and to observe the temperature of the ice a platinum wire of resistance 1·32 ohms at 0° C. was frozen in the ice and surrounded the condenser. Table VIII. gives the results. K the capacity as given by the resonance experiments with frequency 2×10^6 was ·00022 microfarad. Adding to this $\int_0^t \frac{1}{c} dt - \frac{1}{c_\infty} t$, we find that at time ·0028 the total capacity is ·0038 at − 30° C., whereas it is for the same time ·0065 at − 18° C. The curves of conductivity are given in fig. 8, and show the same character of results as those in the case of glass, fig. 7.

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* THWING finds 2·85 to 3·36; BLONDLOT 2; PERROT 2·04.

Fig. 8.

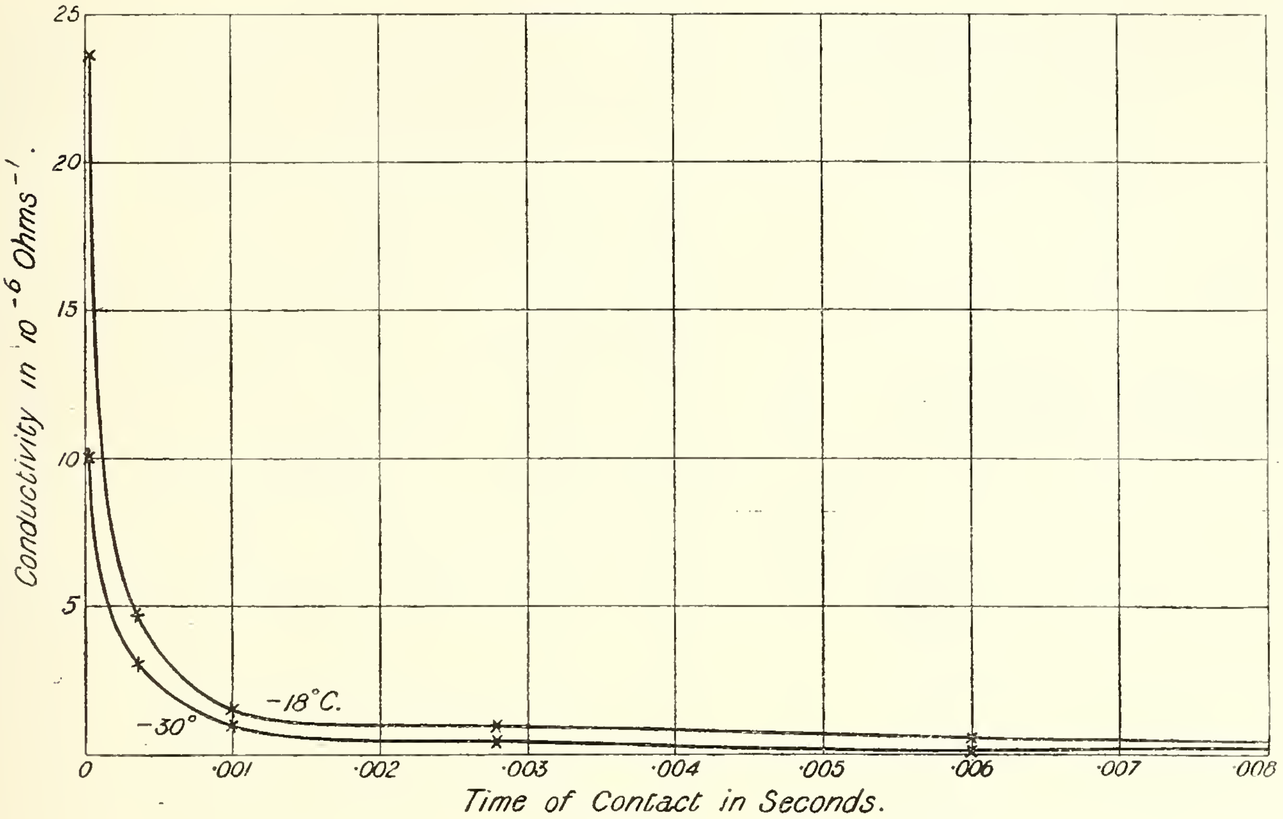


TABLE VI.

Time in seconds.	About − 18° C.	About − 30°.	Remarks.
10	2800	866	Charging volts 890. 8th December, 1894.
20	760	314	Duration of charge, $\frac{1}{4}$ minute in each case.
60	377	74	Resistance at 945 volts.
90	347	44	− 18° C., 7·2 × 10^6 ohms; − 30°, 32·5 × 10^6 ohms.

TABLE VII.

8th December, 1894, − 18° C. about.		8th December, 1894, − 30° C. about.	
Frequency.	Capacity.	Frequency.	Capacity.
77·6	·01	77·6	·0072
10	·019	9	·01

TABLE VIII.—Ice. 5th November, 1896.

a = Resistance box.
K_1 = $\frac{1}{3}$rd *m.f.*
K_2 = Large slide condenser.
K = Instantaneous capacity of ice condenser = ·00022 *m.f.* See Resonance, 19th November, 1895.

Time of contact.		Temperature of Ice, − 18° C.								
					Resistance of Condenser c in 10^6 ohms.			$\int \frac{1}{c}\,dt - \int \frac{1}{c_\alpha}\,dt$.		
Turns of milled head.	Time in seconds.	Large slide position K_2.	a in 10^6 ohms.	$\epsilon^{-\frac{t}{a\mathrm{K}}} = \mathrm{A}$.	From $\frac{a + \mathrm{A}c}{a + c}$.	From $a\frac{\mathrm{K}_1}{\mathrm{K}_2}$.	$\frac{1}{c}$ in 10^{-6}	Area in square centims.	*m.f.*	$\mathrm{K} + \int \frac{1}{c}\,dt - \frac{1}{c_\alpha}t$ in *m.f.*
0	·00002	430	·00019	10^{-200}	·0424	·0424	23·6			
			·00022							
$\frac{1}{2}$	·00035	430	·00096	..	·214	·214	4·67	16·8	·0034	·00362
			·0010							
1	·00099	430	·003	..	·669	·669	1·49	25·15	·005	·00525
			·003							
2	·0028	430	·0059	..	1·32	1·32	·758	31·4	·00628	·00650
			·0060							
3	·006	430	·0078	..	1·74	1·74	·575	37·4	·0075	·00772
			·0079							
4	·009	430	·0095	..	2·12	2·12	·472	39·2	·0078	·00802
5	·011	430	·011	..	2·45	2·45	·408	40	·008	·00822
			·011	..	*2·45*	*2·45*				
6	·014	..	·011	..	2·45	2·45	·408	40	·008	·00822
7	..	..	·012	..	2·68	2·68	·373	40	·008	·00822
			·013	..	*2·90*	*2·90*	*·345*			
9	..	*430*	*·013*	..	2·90	*2·90*	*·345*	40	·008	·00822
The italics give the result of a second experiment.										
		Temperature of Ice, − 32° C to − 27° C.								
0	·00002	430	·00045	$1/7 \times 10^{-86}$	·100	·100	10			
$\frac{1}{2}$	·00035	430	·0015	..	·334	·334	2·99	9·3	·00186	·00208
1	·00099	430	·005	..	1·12	1·12	·893	14·2	·00284	·00306
2	·0028	430	·014	..	3·12	3·12	·320	17·9	·00358	·00380
3	·006	430	·021	..	4·68	4·68	·214	22·4	·0045	·0047
4	·009	430	·0255	..	5·69	5·69	·176	23·9	·0048	·0050
5	·011	430								
6	·014	..	·032	..	7·13	7·13	·140	25·1	·0050	·0052
8	..	430	·039	..	8·7	8·7	·115			
10	..	..	·043	..	9·59	9·59	·104			
11	..	430	·045	..	10·0	10· 0	·100			

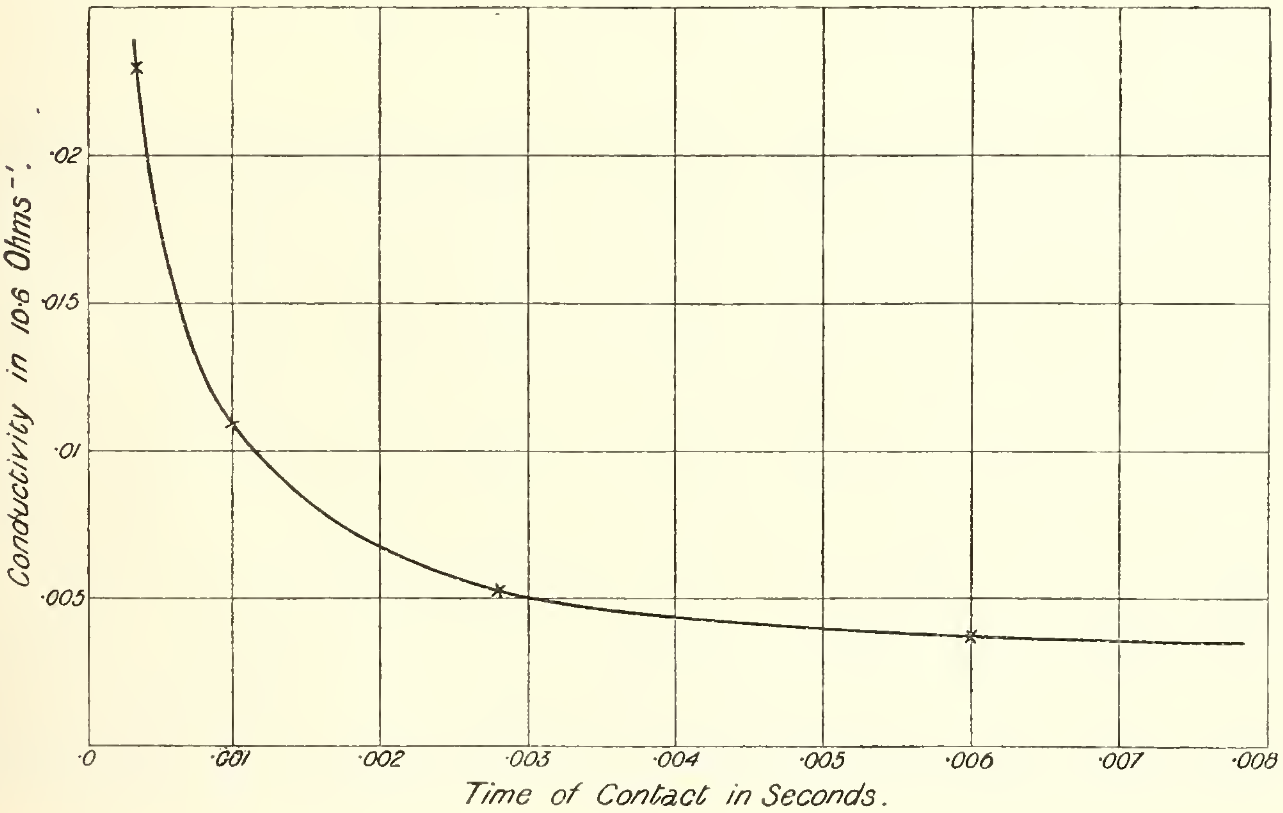
[Added January 18th, 1897.]

Castor Oil.

This oil was obtained from Messrs. Hopkin and Williams, and was tested as supplied. The platinum plates, fig. 2, were submerged in this oil. Resonance experiments give, for frequency 2×10^6, a capacity equal to 105 divisions on the large slide condenser. For long times the method was not that shown in fig. 3, but a bridge method, used in the earlier experiments,* in which a Ruhmkorff coil is used for exciting. This test gives 139 scale divisions on the same slide condenser. In air the plates have capacity 30 scale divisions. We see, therefore, that at frequency 2×10^6 the specific inductive capacity would be 3·5 as against 4·63 for long times.

The short-time contact experiments, fig. 5, give the results in Table IX., the temperature of the oil being 6°C, from which we see that residual charge in this oil is considerable. The total capacity after time of contact ·006 second is ·00034; whereas, with high frequency by resonance, it is ·000287 microfarad. The curve in fig. 9 gives the relation between conductivity and time of contact, and has been plotted from Table IX.

Fig. 9.



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* See 'Proc. Roy. Soc.', vol. 43, p. 156.

TABLE IX.—Castor Oil. 16th November, 1896.

$K_1 = \frac{1}{3}$ microfarad Condenser; K_2 = large slide Condenser.
K = ·000287 microfarad from High Frequency Resonance Experiment.

Time of contact.		Temperature of Castor Oil, 6° C.							
Turns of milled head.	Time in seconds.	Large slide position K_2.	a in 10^6 ohms.	$\epsilon^{-\frac{t}{aK}} = A$.	Resistance of Flask c in 10^6 ohms.		$\frac{1}{c}$ in 10^{-6} $(l^{-1}t)$.	$\int \frac{1}{c}dt - \frac{1}{c_\infty}t$.		$F = K + \int \frac{1}{c}dt - \frac{1}{c_\infty}t$ in $m.f.$
					From $\frac{a+Ac}{a+c}$.	From $a\frac{K_1}{K_2}$.		Area in square centims.	$m.f.$	
0	·00002	430	·015	1/100	− 2·7	3·34	·3*			
$\frac{1}{2}$	·00035	160	·095	1/361000	43·1	43·1	·023	6·2	·000025	·00031
1	·00099	40	·110	..	..	92·7	·0108	8·5	·000034	·00032
2	·0028	40	·223	..	..	188	·0053	12	·000048	·00033
3	·006	40	·320	..	..	270	·0037	14	·000056	·00034
5	·01	40	·460	..	..	388	·00258			
7	..	40	·620	..	..	523	·0019			
9	..	40	slightly greater than ·620							

GLYCERINE.

This glycerine was obtained from Messrs. HOPKIN and WILLIAMS, and has been tested for purity and dried very carefully by Mr. HERBERT JACKSON, of the Chemical Department of King's College, London. The platinum plates, after careful cleaning in benzene, caustic-potash, and water were thoroughly dried and submerged in the glycerine in a beaker, the whole being placed in a glass receiver over a strong dehydrating agent. After exhaustion, just sufficient air was admitted to render the space inside sufficiently non-conducting to stop discharge between the terminals of the condenser which are sealed into glass tubes supported by an indiarubber stopper. The short-contact experiments show that the apparent resistance is 60,000 ohms, whether the time of contact be ·00002 or ·001 second, showing that there is no residual charge. The resonance experiments with high frequency give ·005 microfarad for the capacity with glycerine, whereas with air the condenser had ·000082 capacity; the specific inductive capacity is, therefore, about 60. A test made as with castor oil with a Ruhmkorff at low frequency was difficult, but a fair approximation was made by introducing a suitable compensating leakage into one of the other condensers of the bridge.* The result indicated a capacity between 50 and 60.

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* Taken from $a\frac{K_1}{K_2}$, since the negative value obtained from $\frac{a + Ac}{a + c}$ is untrustworthy, probably owing to K being still too large. To satisfy MAXWELL'S law, K should = ·000176 microfarad.

WATER.

The platinum plates (fig. 2) were placed in ordinary distilled water in a beaker which was cooled to 0° C. by a surrounding brine solution composed of water, common salt and ice. The experiments with the short-contact apparatus show no material difference in the apparent resistance, whether the time of contact be ·00002 or ·00099 second; the apparent resistance for these times is 379 ohms. The effects of residual charge in water do not affect the resistance within the range of times of contact given by this apparatus.

[Added March 17th, 1897.]

OIL OF LAVENDER.

This oil was supplied by Messrs. HOPKIN and WILLIAMS: it was tested with the short-contact apparatus, fig. 5, $K_1 = \cdot 33$, $K_2 = \cdot 0015$ microfarad. The charging potential was 1250 volts; the following figures give the results:—

Time of contact in seconds . .	·00002	·00099	·0028	·006	·01
a in ohms	9500	14000	14500	14800	14800

The high frequency resonance experiments give specific capacity 3·89: the frequency being of the order 2×10^6.

Two experiments were made at low frequency. First, the Bridge method, fig. 3, which gives the following results, the temperature of the oil being 16°C.:—

FREQUENCY	Charging	Specific.
	Volts.	Capacity.
18	65	5·6
79	30	4·34

Second, the Bridge method with Ruhmkorff coil as used in the castor oil experiments. Temperature 14°C. Specific capacity 4·18.

Experiments have been made by STANKEWITSCH ('Wied. Ann.,' 52), showing a variable capacity for oil of lavender. We, however, have not succeeded in obtaining any result so high as his.

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* This appears to have been done by NERNST, 'Physical Society's Abstracts,' vol. 1, p. 38.

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V. *Impact with a Liquid Surface, Studied by the Aid of Instantaneous Photography.*

By A. M. Worthington, *M.A., F.R.S., Professor of Physics, Royal Naval Engineering College, Devonport, and* R. S. Cole, *M.A.*

Received September 25, 1895,—Read February 6, 1896.

[Plates 1–8.]

Preliminary Statement by Professor Worthington.

In three papers, published in the 'Proceedings'* of the Society, in 1877 and 1882, I had the honour to communicate to the Society the results of experiments on various classes of impact with a liquid surface which may all be conveniently referred to as "splashes." The splashes studied were those produced (i.) by a liquid sphere falling on a horizontal solid plate, (ii.) by a liquid sphere falling into a liquid, (iii.) by a solid sphere falling into a liquid.

The phenomena were examined by means of an electric flash of very short duration, which by a suitable mechanism could be so timed as to illuminate the splash at any stage which it was desired to observe, within three or four thousandths of a second. After a sufficient number of repetitions to secure accuracy, a drawing was made of the configuration thus revealed, and when one stage had been sufficiently studied, the observer passed on to a later stage. Since, however, each drawing was made from a separate, though similar splash, it was not possible to obtain accurate information about those details which were at once too minute to be seized in such single, momentary glimpses, and too unstable to be capable of exact reproduction in another splash.

A photograph, which can be studied at leisure, is under such circumstances indefinitely more valuable than a drawing, and produces that confidence in one's knowledge of the facts without which speculation as to the causes can hardly proceed. But, at the date when the observations were made, photographic plates, sufficiently sensitive to respond to such extremely short exposures were not obtainable, and my efforts to secure photographs were unsuccessful. A year and a half ago, encouraged by Professor Boys's success in the photography of flying bullets, I returned to the attempt, being also so fortunate as to obtain the co-operation of my colleague at

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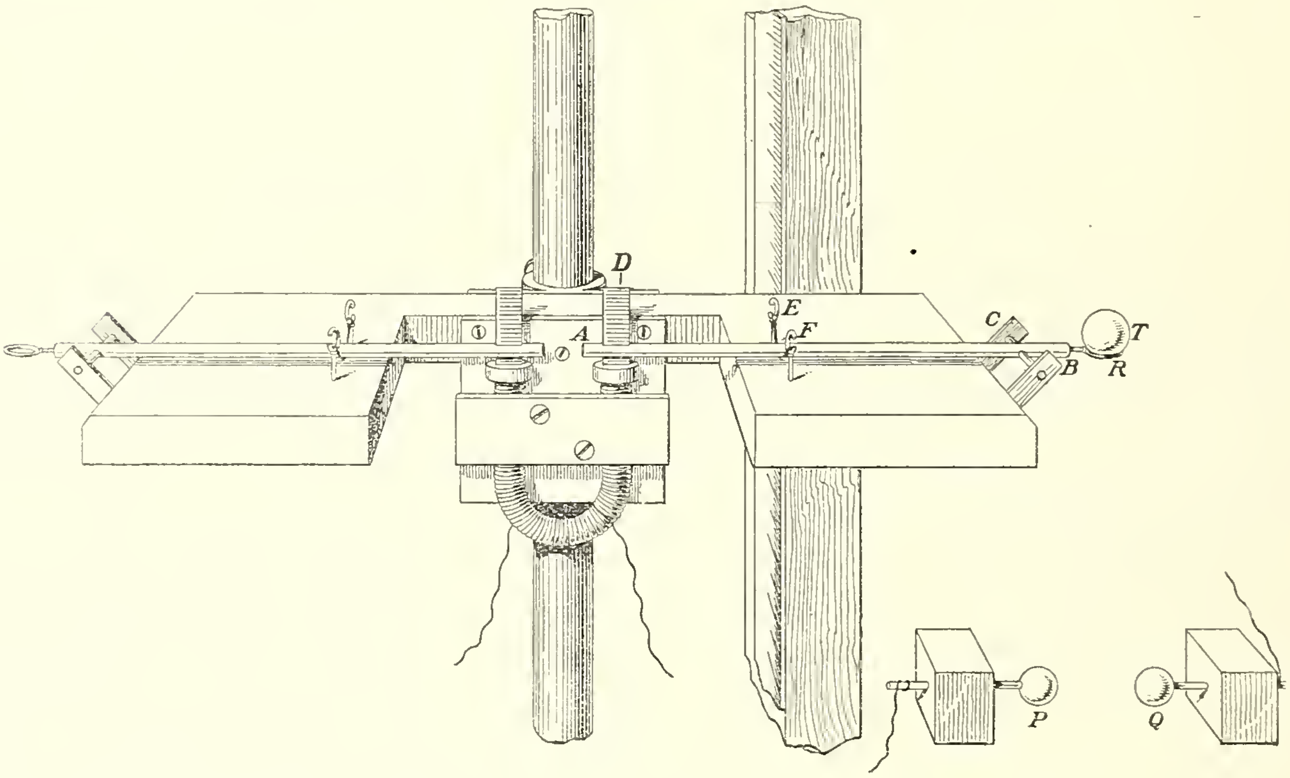
* 'Proc. Roy. Soc.,' 1877, vol. 25, pp. 261 and 498, and 1882, vol. 34, p. 217.

Devonport, Mr. Cole, and after taking advice from Professor Boys, and exchanging my old self-induction spark for the much shorter Leyden-jar spark that had been employed by Lord Rayleigh* for a similar purpose, we obtained after a few weeks of failure, some preliminary photographs which were shown at the Royal Institution, May 18, 1894.† These photographs, while amply confirming the old drawings, gave so much new and detailed information as to make it seem worth while to go over the whole ground again. Of this review, which is our joint work, the following communication is the first instalment.—A. M. W.

Fig. 1.



Method of Taking the Photographs.—The method consists in letting fall, simultaneously with the drop, a metal timing-sphere. This in its fall passes between two other insulated spheres connected to the inner coats of two large, oppositely-charged Leyden-jars that stand on the same badly-conducting table. From the outer coats of these jars wires are led into the dark room, and there terminate in a spark-gap between magnesium terminals at the focus of a small concave mirror. The timing-sphere, in its fall, discharges the inner coatings of the two Leyden-jars, and this produces a simultaneous discharge at the spark-gap between the outer coatings, and it is this that illuminates the splash.

Fig. 1 is a magnetic releasing key, of which two were used on the same electric circuit, one in the dark room for releasing the drop or sphere whose splash is to be photographed, and the other in the laboratory for releasing simultaneously the timing-sphere.

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* See 'Nature,' July 16, 1891, p. 249.

† 'On the Splash of a Drop and Allied Phenomena'—a Friday Evening Discourse. This will be found to contain a *résumé* of all previous papers. See also in 'Nature,' July 5, 1894, a paper by Mr. Cole.

A B is a light wooden rod, about 20 centims. in length, and rather stouter than a lead pencil; this is pivoted at C. At the end B is fixed a metal ring (R), on which the timing-sphere (T) can be placed. At the other end (A) is fixed a thin strip of tinned iron plate (D), which is held down by the electromagnet beneath it against the pressure of a catapult made of an indiarubber ring stretched between the two hooks E and F. On cutting off the current of the electromagnet, the end A is tossed up by the catapult, and thus T is left in mid-air free to fall from rest. The end B is prevented from rebounding, and thus possibly interfering with the fall of T, by impaling itself on a suitably placed pin, which is hidden from view in this diagram, but is seen at H in fig. 2.

The releasing key in the dark room is precisely similar to this, with the exception that when a liquid drop is to be let fall it carries, instead of the ring R, a small and deeply concave watch-glass, on which, when well smoked, a drop of milk or water will lie with little or no adhesion.

On breaking the circuit of the two electromagnets the drop and timing-sphere are thus simultaneously released, and the former makes its splash at the moment that the latter, by passing between the fixed spherical terminals P and Q, insulated by supporting blocks of paraffin wax, discharges the Leyden-jars.

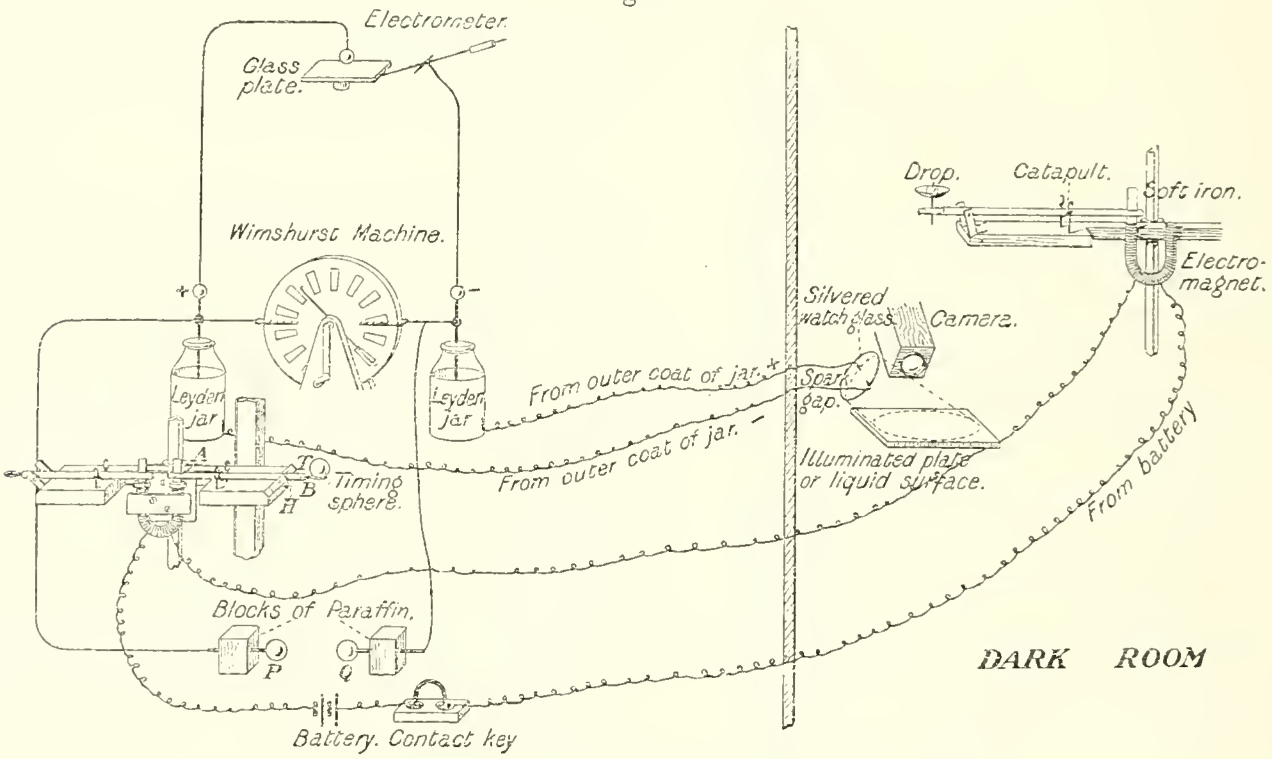
The timing of the spark is effected by adjusting the height of fall of the timing-sphere, which is done by sliding the releasing key up or down its vertical supporting rod, the height being read off on a millimetre scale which was pinned against a firmly fixed and well planed, oak batten.

The general arrangement of the apparatus is shown in fig. 2.

It will be noticed that on the left-hand side of either figure there is an idle releasing lever. This projected over the edge of the table, and was used instead of the right-hand lever when the height of fall was more than about 2 metres, the paraffin blocks carrying P and Q being then put on the floor. Instead of the rough electrometer figured, a pith ball, hanging by a cotton-thread from the upright stem of one of the jars, was more frequently employed to show the extent to which charging had proceeded, of which also the sound of brush discharges was a useful indication, for, in order to secure a bright spark, we generally charged the jars up to the limit determined by leakage.

Photographic Apparatus and Details.—The chief necessity is to secure adequate illumination, and for this as little light as possible must be wasted. After many trials the difficulty was successfully met by using as a mirror a concave watch glass of a width about equal to that of the area to be illuminated, and very approximately parabolic in form and sufficiently deep for the focus to be very nearly in the plane of its circular edge. This glass was found to be sufficiently "silvered" by means of a sheet of thin tinfoil rubbed smooth over the inside, and renewed occasionally after it had become too much dimmed by magnesium oxide. This mirror, with the sparking wires close in front of it, was brought within 8 or 9 centims. of the place of impact, and, in order to bring out the details of the configuration to the greatest advantage, the beam of light was directed down on the surface at an angle of between 30° and 45° with the horizontal, and the camera was so placed that the line of sight was at right angles to the plane of incidence of the axis of the illuminating beam, and also inclined at about 30° to the horizontal (fig. 2).

Fig. 2.



Arrangement of apparatus for photographing splashes.

The camera employed was an ordinary quarter-plate camera. For our earlier observations the ordinary camera lens was exchanged for a single quartz spectacle lens with the object of avoiding the absorption of useful actinic rays by glass. This, however, gave imperfect definition in parts of the field away from the centre, and the position of the best actinic focus was also troublesome to find. And we soon found that the illumination was amply sufficient for the ordinary lens. This had a focal length of 15 centims. and was used with full aperture of 2·22 centims., and placed at such a distance from the splash as to give an image three-fourths (linear) of the real size.

The plates used were THOMAS's cyclist, and were developed in complete darkness by treatment with a saturated solution of eikonogen for about 40 minutes, according to the advice kindly given us by Professor BOYS.

In order to identify the photographs it was necessary to number the negatives, and, to escape the difficulty of doing this in pitch darkness by scratching the film or otherwise, we adopted the plan of "numbering the phenomenon" by means of a ticket which was photographed simultaneously.

The Duration of the Spark.—Although it was not necessary for the success of our experiments that the spark should be excessively short, yet we cannot doubt that its effective duration was less than three-millionths of a second. This was ascertained by photographing by its means a cardboard disc, 22 centims. in diameter, roughly graduated round its edge with pen and ink, and kept rotating by means of a small electromotor at a rate of between 52 and 54 revolutions per second. This rate of rotation was ascertained by smoking the back of the disc and touching it with a style attached to an oscillating tuning-fork, or with the fork itself, and the result was confirmed with a second fork. The edge of the disc was thus found to be moving at about 36·5 metres per second (or about 78 miles per hour) during exposure, yet no trace of motion is apparent in the photographs. A motion of one-tenth of a millimetre during illumination would correspond to less than three-millionths of a second, and would have produced in the photographs a blurring of three-fourths of one-tenth of a millimetre which, with a lens, would certainly be visible. This interval of less than three-millionths of a second bears to one second just about the same ratio as a day to a thousand years.

Although the outside limit thus obtained is 30 times greater than the effective duration of the spark employed by Professor BOYS with his flying bullets, yet we think it worth while to mention the result, for it shows how excessively short is the exposure necessary for taking even very detailed "objective views" as distinguished from shadow photographs requiring no camera.

It may be mentioned here that the illuminating spark-gap was sometimes as much as 3·3 centims. wide; that the two jars were of not quite equal capacity, the lesser consisting of a set of jars and presenting an area of about 4000 sq. centims. and a mean thickness of dielectric of about 0·3 centim., while the potential difference was such as would make a spark leap across from P to Q when the distance between them was about 3 centims., P and Q being spheres of 2 centims. in diameter.

The Accuracy of the Timing.—The interval between the release of the drop and the production of the illuminating spark is liable to slight variation, chiefly from two causes—(i.) irregularity in the potential difference between the two terminals P and Q, on account of which the spark would leap through varying distances to meet the timing sphere before it reached the line of centres, and (ii.) want of consonance in the rates of demagnetization of the two magnets. Thus, after long running, one magnet would get hotter than the other, and again an alteration in the strength of the magnetizing current was found to shift slightly the stage of the splash revealed by the spark. Nevertheless, after allowing the current to run for a few minutes, and after taking a few preliminary discharges, a condition of affairs was reached so steady that changes in the height of fall of the timing-sphere corresponding to intervals not greater than 2 or 3 thousandths of a second, produced a very steady progress through the phenomenon, and in four test experiments that were made by photographing a solid sphere falling past a divided scale, three consecutive trials, made under ordinary good conditions, agreed within $\frac{1}{3000}$ second, while the fourth was not in error by as much as $\frac{1}{1000}$ second.

When, however, the splash, not of a solid sphere, but of a falling *drop* was being observed, a further cause of irregularity was introduced by the oscillations set up in the drop itself on its release, and by the slight adhesion between it and the supporting watch-glass. This adhesion is proved in the case of a water drop by its invariably carrying down with it a little lamp-black from the smoked surface. A drop of milk, on the other hand, carried down very little, and on this account, and probably also because of the greater viscosity of milk, the splash of a drop of milk is less troublesome to follow in its initial and most rapidly changing stages than is that of a drop of water. We had also reasons to suspect that after setting a drop in place on the watch-glass the film of intervening air gradually escaped and led to a suctional adhesion if the release were too long postponed. Dusting the watch-glass, after smoking, with lycopodium powder appeared to diminish the adhesion.

Nevertheless, when care was taken to preserve regularity in the procedure, the same one of us always manipulating the Wimshurst machine and the laboratory releasing key, and the other the dark-room releasing key and the setting of the drop in place, the apparatus worked and worked well, and if the steps taken between the photographs of a series are as much as $\frac{3}{1000}$ of a second, reversals of the proper order will be exceptional, and there is no difficulty in obtaining stages at closer intervals if desired.

We found, however, that between series of photographs taken on different days there were sometimes noticeable breaches of continuity in the timing, which may be attributed to changes in the potential difference between P and Q, and therefore in the distance from them of the timing sphere when the flash took place, and perhaps to other causes that escaped our notice; we have consequently distinguished photographs taken on different days by letters placed just above the right-hand corner.

For the rest it may be observed that it has not yet seemed worth while to press the accuracy of the timing much beyond what is required for a complete record of the consecutive phenomena.

No misapprehension can arise as to the times assigned, if it is remembered that they refer to the setting of the apparatus, and are liable to such uncertainties as have been mentioned.

The Photographs.—Series I. (Plate 1), consisting of 33 photographs, gives the splash of a water drop, weighing ·2 of a gram.,[*] falling 40 centims. into milk mixed with water, scale $\frac{3}{4}$ of actual size (linear). The first 7 or 8 show the evolution and rise of the crater to its maximum height, which is attained in about two hundredths of a second; this crater then remains poised with but little change for another hundredth of a second (figs. 8 to 12), and then (figs. 13 to 20) in about two and a half hundredths more widens out and subsides till nothing but a lobed rim is left above the surface surrounding a central hollow (fig. 20). This is followed by the rise of a central column carrying the liquid of the original drop on its summit. The distinction between the more transparent water at the top and the comparatively opaque adherent milk below is quite observable in the original of Photograph (22) though hardly apparent in the reproduction, and, in all, the lamp-black carried down by the drop is seen to be collected chiefly at the summit. The rise of the column takes about $\frac{5}{100}$ second (figs. 21 to 26), and its subsequent subsidence (figs. 27 to 29) about $\frac{7}{100}$ second more. In Photograph 24 is seen the first appearance of an outward-spreading ripple. Photographs 26 to 30 show how the base of the column gradually flattens down into a "cake" of liquid, whose edge marks the position of the next well-marked ripple, while figs. 31, 32, and 33 show how by the oscillations of the centre, a third "cake" is superposed on this, contributing the third outward-spreading ripple and so on. We were not able conveniently to follow the phenomenon further, through the laboratory being too low for the height of fall necessary for the timing-sphere at these late stages.

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[*] Drops of a constant size were obtained from a vertical glass tube, connected by indiarubber tubing, with a wide funnel, in which the level was slightly higher than the mouth of the delivery tube. The experimental drop was made up of a definite number (1, 2, 3, or 4) of such drops, caught in a smoked and lycopodium-dusted watch-glass and thus conveyed to the releasing cup.

It should be mentioned that it is known (WORTHINGTON, 'Proc. Roy. Soc.,' 1882, vol. 34, p. 217) that the subsidence of the central column gives rise to a vortex ring that descends through the liquid.*

The reason for mixing milk with the water into which the drop fell was to secure something which would photograph. It was found that the addition of milk in the proportion of about one part of milk to three of water, though it must have reduced the value of the surface tension, did not make any decided or very noticeable change in the phenomena. If pure milk was used the crater thrown up was indeed somewhat higher and had longer arms, indicating a smaller efficiency of the surface tension in opposing the rise of the liquid.

Series II. (Plate 2).—This gives, in 37 photographs, the splash of a milk drop of diameter ·75 centim. (*circa*) falling 100 centims. into water. Scale $\frac{2}{3}$ linear, as far as No. 18 (the single quartz lens being used). Thence onward $\frac{3}{4}$ linear (with the ordinary lens of the camera). In Nos. 15–18 a little milk was added to the water to make the photographs clearer, and from 19 onward a good deal of milk (about one part of milk to three of water). In this splash the crater rises to a greater height and closes completely over the central hollow, opening again, however, very shortly afterwards to make way for the column that rises from the base, and whose subsidence produces "cakes" as before. In Photograph 18 the bubble has apparently not yet burst before its top is struck by the column rising inside. Sub-group A consists of special studies showing the bubble opening quite centrally round the emergent column, and the fact that the base of this does not photograph shows how completely the original milk drop is collected at the top of the column. Sub-group B illustrates what happens when, as in Photograph 18, the top of the bubble is struck by the column and burst at one side. Under the influence of the surface tension, rotundity of form is soon regained, and by the time the stage of Photograph 21 is reached all traces of previous irregularities have disappeared.

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* See also THOMSON and NEWALL, 'Proc. Roy. Soc.,' 1885, vol. 39, p. 417.

Examination with a lens of Photographs 3, 4, and 5 shows how the drop, on first entering, punches a very sheer-walled hole.* From the fact that these early stages photograph so well as compared (see next series) with corresponding stages when the drop is of water and the liquid is milk, we infer that the first liquid thrown up is milk drawn from the fringe of the drop itself. It must be remembered that owing to the closeness of the camera, front and back parts of the crater cannot be quite in focus together. The first flow of the liquid appears to be very much *along* the surface, afterwards it is much more perpendicular to the surface, and this alone appears sufficient to account for the sharp curling-over of the edge of the crater (Photographs 4 to 6); for superposition of the photographs seems to show that in the early stages each particle continues to move for some distance in the straight line along which it was first projected from the surface. As to the reason of the closing in of the crater we shall make some remarks in connection with the next series.

Series III. (Plate 3).—This gives, in 24 photographs, the splash of a water-drop weighing ·4 gram. falling from a still greater height, 137 centims., into milk mixed with water. Taken with the quartz spectacle lens. Scale $\frac{1}{2}$ linear. The crater closes up at a much earlier stage and forms a bubble which becomes smoother in outline as the liquid drains down its sides or distributes itself more evenly over its walls. This bubble may remain closed (Photograph 16) or may open at a comparatively early stage, following the course shown by Photographs 13, 14, and 18. Or it may be from the first much depressed by the heavy mass of liquid at its top (Photographs 11, 15, and 17). Sub-group A shows the configurations of early stages when the water-drop is exchanged for an equal drop of milk and falls into water. The increase in visibility is very marked. The original of No. 1A bears examination with a lens. In Sub-group B the crater obtained was smaller than usual, perhaps through the drop striking the water in a very prolate form, as in Series I., Photograph 1.

With respect to the closing-in of the crater, it will be noticed that in Photographs 6, 7, and 8, the upper edge is surmounted by a rim of greater thickness than the walls below; there can be no doubt that the accumulation of liquid here is due to the upward flow being checked by the surface tension. When such an annular rim is formed, an elementary calculation shows that the centripetal acceleration with which it will contract under the influence of the surface tension exceeds the inward acceleration of the cylindrical walls of the crater arising from the same cause, so long as the diameter of the rim is less than 1·61 of the thickness of the wall. Although this must be a *vera causa* in determining the more rapid contraction of the upper portion of the crater, yet it may not be the sole cause. Photograph 8, and particularly Photograph 2_b, of the sub-group suggest that there may be a diminution of air-pressure within the crater, owing to the descent of its base whereby the crater is in part forced in by excess of external air-pressure. (See also, with a lens, Photograph 5 of Series IX.)

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* So much of the detail of the original photographs has been lost in the reproductions that it is only in fig. 5 that the edge of the vertical cliff of liquid is visible at the far side of the crater. This edge marks the free horizontal surface of the, as yet, undisturbed liquid.

It appears to be characteristic of all closing bubbles that the arms are inclined outwards (see also Series II. and IX.), as if they were being dragged in by the contracting rim from which they spring. In an opening bubble they are much more erect (Series III., 13 and 14), or even inclined inwards (No. 18). A late stage in a bubble is also differentiated from an early one by the greater smoothness of its surface, and by the absence of very small drops in air above it, such smaller drops having apparently had time to agglomerate into larger.

Splashes of Solid Spheres.—The remaining Series exhibit the splash of solid spheres. It was already known (WORTHINGTON, 'Proc. Roy. Soc.,' 1882, *loc. cit.*) that the disturbance set up by a very smooth and well-polished sphere is quite different from that due to the impact of the same sphere when rough or wet, and it is a matter of great interest to find that the difference is quite pronounced from the first instant of contact.

Series IV. (Plate 4) gives, in 17 photographs, the splash of a well-polished sphere of ivory, 1·9 centim. in diameter, falling 60 centims. into water mixed with milk, contained in a glass bowl about 1 foot deep and 9 inches in diameter (scale $\frac{3}{4}$ linear). In order to secure that the splash shall follow the lines here recorded, the polishing with a dry cloth or wash-leather must be repeated just before each observation, and after this the sphere must be handled as little as possible ; with these precautions a stone sphere behaves in just the same way. Photographs No. 2 and No. 3* show that the liquid rises over and surrounds the sphere with a thin close-fitting sheath. Figs. 5 and 6 show a subordinate side-sheath, which, without doubt, was due to the fact that the sphere had a crack in it, which occasionally carried down air with it, and disturbed the symmetry of the splash. In Photograph No. 7, however, the symmetry is complete, and it is nearly so in Photograph No. 8. When any failure of the polishing occurs, the liquid is kept away from the sphere, and the splash, instead of being almost noiseless, is accompanied by a sound of bubbles rising to the surface and bursting. Photograph No. 4 shows this driving away of the liquid, and our note-book records that this splash was attended by "noise, bubbles," &c. In Photograph No. 8 there is a similar sign of roughness on the right-hand side. Very important is the information given by the shadow thrown across the surface in such figures as 8 and 9.

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* The light marking on the right side of Photograph No. 3 is due to a flaw in the negative.

The sphere has passed below the surface, yet this is almost undisturbed, and there is no trace of the equivalent quantity of displaced liquid. Indeed, in Photograph No. 9 (as in Photograph No. 3 of Series V.) there is an indication of a slight depression surrounding the small column. The conclusion we arrive at is that the general level of the whole liquid surface rises simultaneously with the entry of the sphere, or, at any rate, after an interval corresponding to the velocity of sound through the liquid. Direct evidence of this will be given later. But the surface, though undisturbed, is no longer the surface of dead liquid. Already in Photograph No. 9, and in the corresponding Photograph No. 3, of the next series, there are traces of convergent radial stream lines, indeed, the slight depression is itself evidence of velocity; in Photograph No. 10, after a relatively long interval, the base of the column has gathered liquid, and Nos. 11, 12, and 13, which are coincident in point of time, show the very considerable column that subsequently rises (No. 13 probably owes its double column to some such antecedent condition as is shown in Photographs 5 and 6). Photographs 15 and 16 show the curious and characteristic manner in which this column topples over, while No. 17 shows how it occasionally succeeds in attaining a more considerable height.

Series V. (Plate 5) shows the similar splash of a rather smaller stone sphere, 1·5 centim. in diameter, falling through the same height of 60 centims. Examination of No. 2, with a lens, shows how, on the front side, the sheath (owing, no doubt, to imperfect polishing) has been driven away from the surface of the sphere, while at the back it has run up almost to the vertex. Of this splash we recorded that "bubbles were heard." Photographs 4 to 9* are all characteristic of the manner in which the column breaks up or topples, and appear to deserve record, if only to help future observers in what is sometimes a rather puzzling identification.

Series VI. (Plate 6) was taken with a large stone sphere 3·2 centims. in diameter, falling only 14 centims. (scale $\frac{3}{4}$ linear), with a view to obtaining further information about the displaced liquid. In Photograph No. 1, the plate was accidentally exposed to a spark beforehand. No. 2 shows very well the rise of the sheath. No. 4 is interesting as illustrating in a very complete manner the influence of some slight roughness on one side only. The puckering of the surface, which is strongly marked in No. 5, seems to us to show that lines of flow near the surface when once determined are very persistent, for we should otherwise expect to find a gradual thickening of the sheath as the vertex is approached, but not these separate radial streams. In No. 6 the general surface is very level, while the amount of liquid in the column can hardly be $\frac{1}{10}$ of the volume of the whole sphere. It still remained, however, just doubtful whether a very gradual sloping-off of the surface might not provide, in a manner not easily noticed, accommodation for a large amount of liquid just round the place of impact. We, therefore, choosing the narrower vessel of No. 8 to make the phenomenon more apparent, filled it brim-full and placed the lower edge of a card millimetre scale, just in contact with the liquid surface at one side. Photograph No. 9 shows the general rise of level due to the entry of the sphere. The rise at the edge of the scale is about 3 millims., but the rise at the spout of the vessel is much more marked, though this is at a greater distance from the place of impact, and the liquid enveloping the sphere seems to rise very abruptly out of the flat surface on this side. We think that all the facts point to rise of level at great distances from the impact even when the vessel is much wider.

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* The dark streak on the left side of No. 9 is an accidental flaw on the plate.

When the ivory sphere, which when dry and well polished gave the splash of Series IV., was allowed to fall *wet* into the liquid, all other circumstances remaining the same, the splash of *Series VII.* (Plate 7) was obtained, which from the very first is entirely different. The wetting was effected by dipping the sphere into the bowl of milky water in which it was to fall and then shaking off as much as possible of the adherent liquid, but in all cases the splash quickly becomes unsymmetrical, probably through the liquid during the fall drifting to one side of the sphere, indeed, in all the figures from 4 onward, but especially in 4 and 5, there is seen a tendency to behave as a smooth dry sphere on the left-hand side where convergent foldings may (in the original photographs) be seen on the surface. The confusion arising from this want of symmetry made it seem unprofitable to examine this splash any further.

This disturbing want of symmetry entirely disappears, however, when we employ a rough sphere, as in *Series VIII. and IX.* (Plate 8). In Series VIII. the impinging sphere was of marble 1·5 centims. in diameter, and the height of fall was 15 centims. The sphere was on each occasion dried and then well rubbed with emery paper. When dipped into the liquid it was at once "wetted" in the usual sense of the term. Yet the liquid on impact seems to do anything but wet it. The first flow is evidently very much along the surface away from the place of impact, and the subsequent behaviour of the crater, as far as Photograph No. 14, is very similar to that of Series I., which was due to the impact of a liquid sphere. Indeed, figs. 8 to 10 of this series hardly differ from Nos. 17–20 of Series I. In the column that afterwards emerges there is, however, a very wide difference. In each case it rises from the bottom of a hollow, but in the present series it is a far finer jet and moving with much greater velocity. This jet was, in fact, observed with the naked eye, in continuous daylight, to rise even to a greater height than that from which the sphere had fallen.

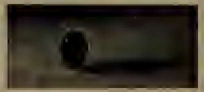
Comparing the crater of this series with that of Series I., we observe that while the outside dimensions are not very different, the crater of the present series is distinctly thinner in the wall, also that the number of lobes or arms is larger. The number seems always to be decided at a very early stage, and to be due, as was suggested (Worthington, 'Proc. Roy. Soc.,' 1882, *loc. cit.*), to the instability of the annular rim. Thus, in Series I., fourteen appears to be a frequently recurring number in the earlier stages, and in Series VIII., twenty-six or twenty-eight, and in both series the number afterwards diminishes, often by coalescence, as the annulus subsides and thickens. This view of their origin appears to gain confirmation from the fact that there is a larger number in the crater with the thinner walls. It is not, however, easy, even from the photographs, to estimate the number very accurately. The reader will best ascertain the nature of the difficulty by trying. Sometimes, on account of the foreshortening of the front rays, these are more easily counted in the image of the crater, that is, reflected by the smooth liquid surface in front of it.

In *Series IX.*, we have the splash of a rough stone sphere, 1·25 centims. in diameter, falling 60 centims., into milky water. Photograph No. 1 shows even better than No. 1 of the previous series the way in which the liquid, from the very first, is driven away from the sphere. The subsequent crater is very like that of Series II. or III. obtained from a liquid sphere, and the manner in which the bubble is formed does not seem to differ materially from the course followed in Series III. It is perhaps doubtful whether the creasing on the left of the neck of the bubble in Photograph No. 5 is due to an excess of external air pressure, as suggested on p. 145, or whether it is a puckering due to radial inflow, as when the sheath closes over a smooth sphere.

This series terminates the record of phenomena that we have at present to lay before the Society. We hope next year to be able to complete the survey, and to obtain information as to what is proceeding below the surface, and to secure also a succession of photographs of different stages of the same identical splash.

It will have been noticed that useful information is yielded by the comparison of one kind of splash with another, and for this reason it appears desirable that the study of each shall be fairly complete and minute. Observations that we have already made on the impact of a drop with a solid surface, seem to throw light on some of the phenomena that are here described.

In presenting the results so far obtained without waiting for a further accumulation, we are influenced by the reflection that there can be, happily, no doubt about the accuracy of the photographic record, and by the hope of eliciting from competent judges some expression of opinion as to the value of the investigation, with suggestions as to the points which it would be most profitable to elucidate. So little seems to be known about the actual behaviour of real, as opposed to imaginary fluids that we cannot but think that trustworthy information about the motions that follow very simple initial conditions may prove of real value, and not of merely curious interest.



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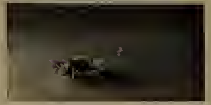

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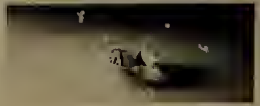

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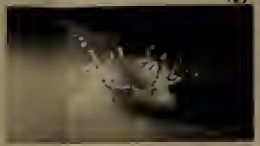

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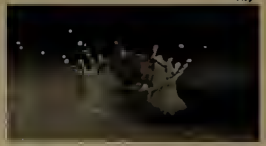

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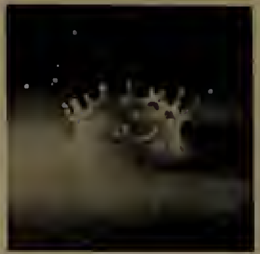

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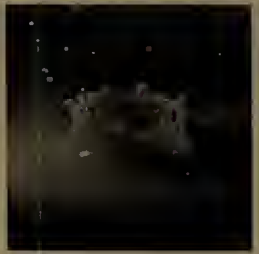

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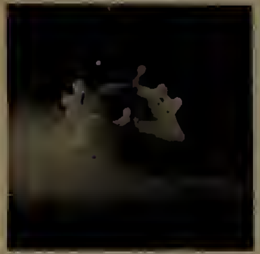

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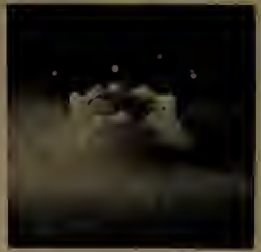

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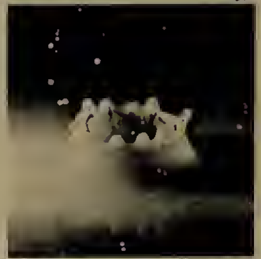

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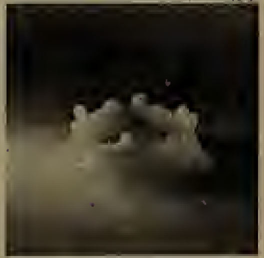

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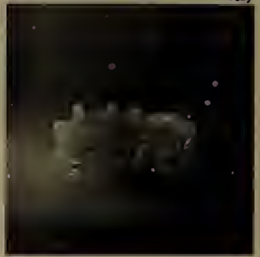

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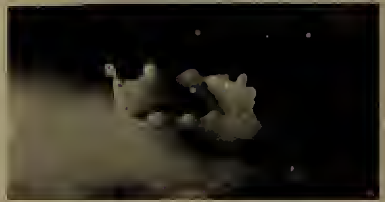

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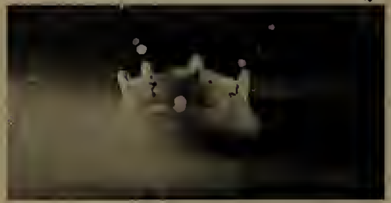

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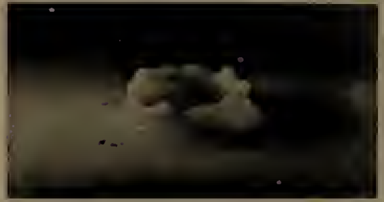

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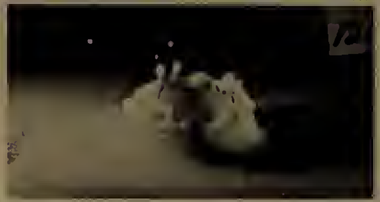

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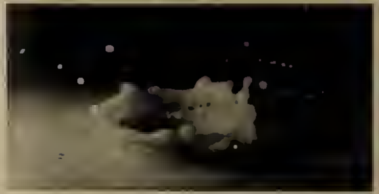

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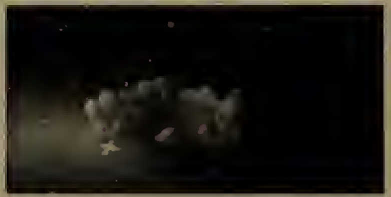

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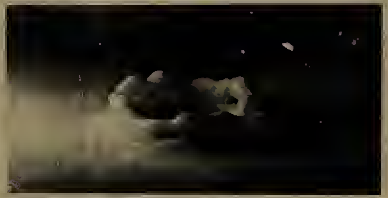
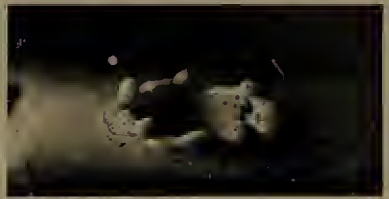


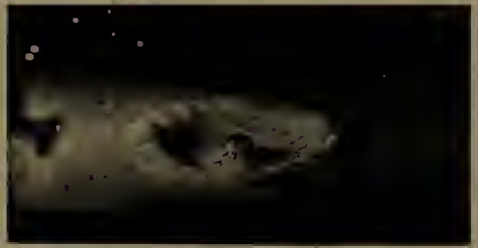
19

t=·0556



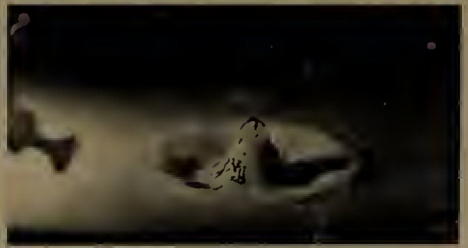
20

t=·0644



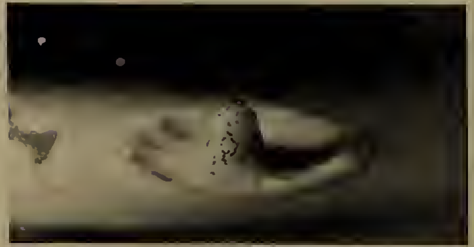
21

t=·0732



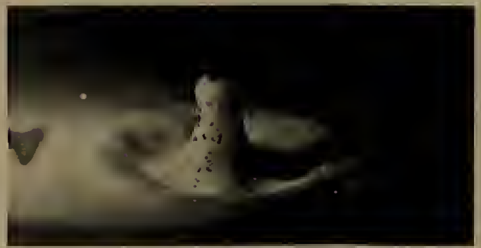
22

t=·0816



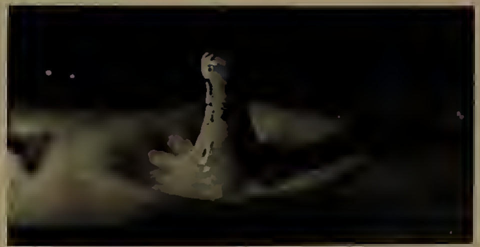
23

t=·0925



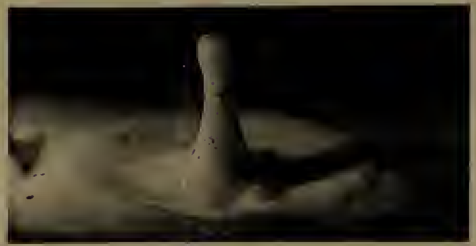
24

t=·1032



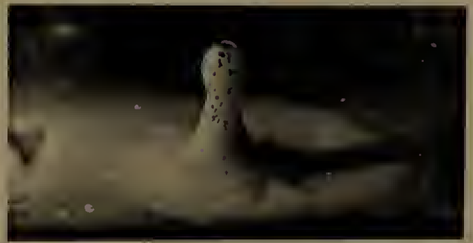
25

t=·1160



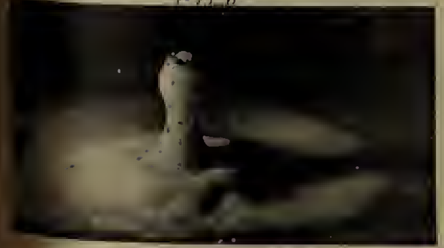
26

t=·1287



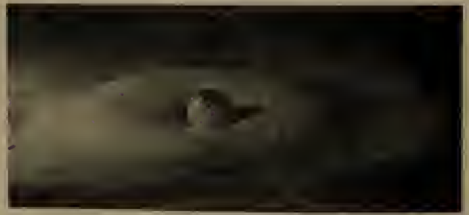
27

t=·1526



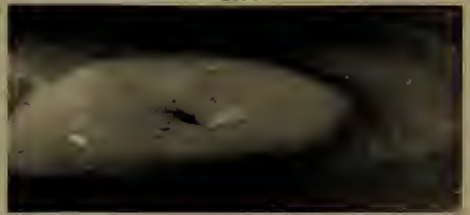
28

t=·1970



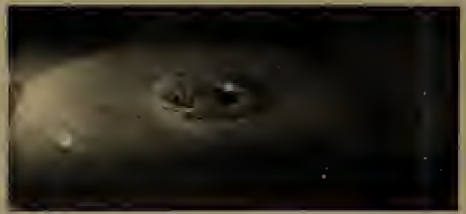
29

t=·2175



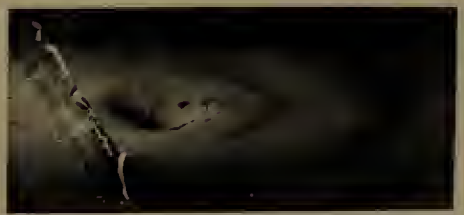
30

t=·2372



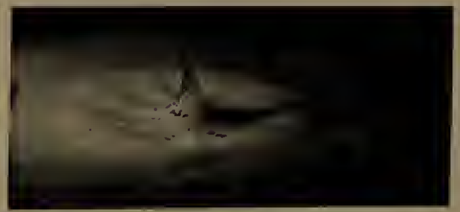
31

t=·2755



32

t=·3107



33

BRITISH MUSEUM
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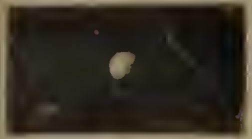
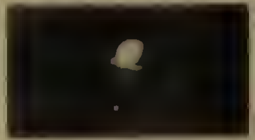
t-0033



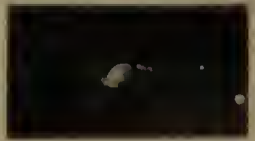
1

t-0045



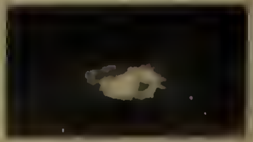
2

t-0



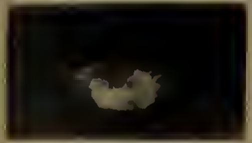
3

t-002 (a)



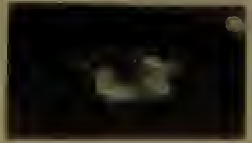
4

t-002 (a)



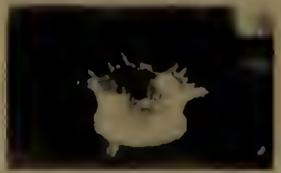
5

t-002



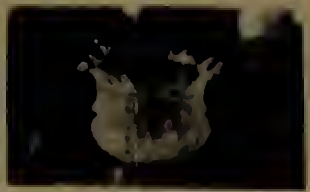
6

t-009



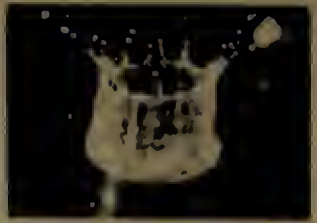
7

t-0133



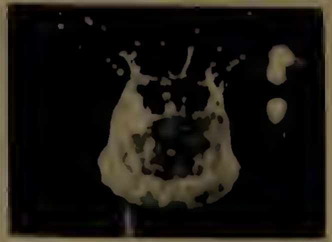
8

t-0179



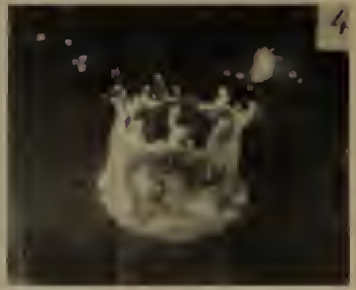
9

t-0179



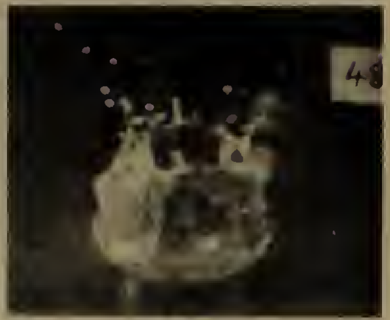
10

t-0245



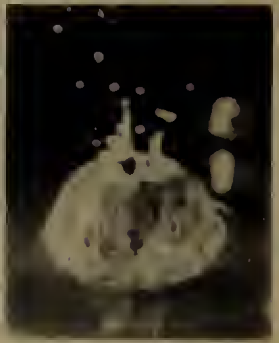
11

t-0331



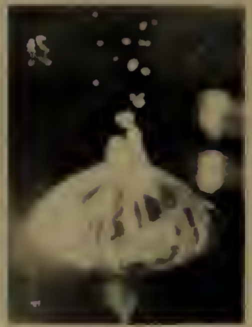
12

t-0394



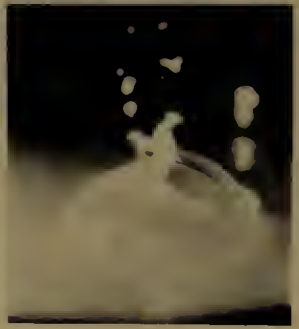
13

t-0538



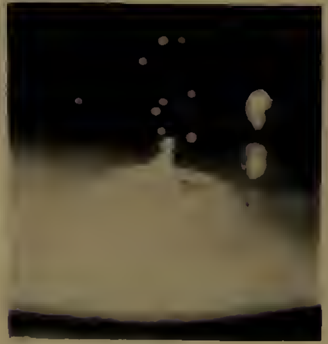
14

t-0677



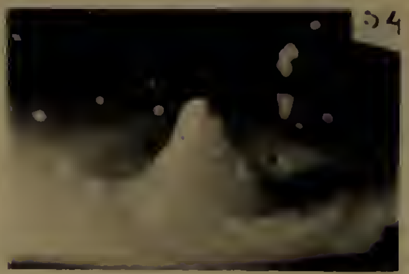
15

t-0854



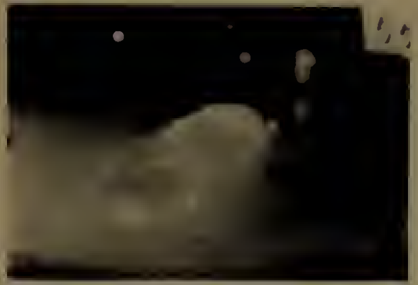
16

t-1045



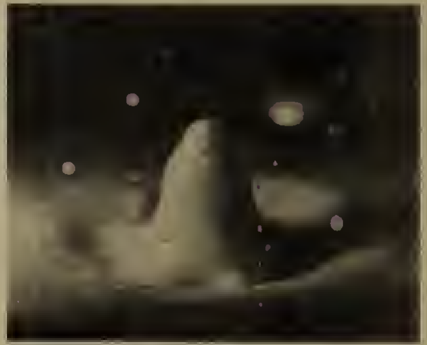
17

t-1045



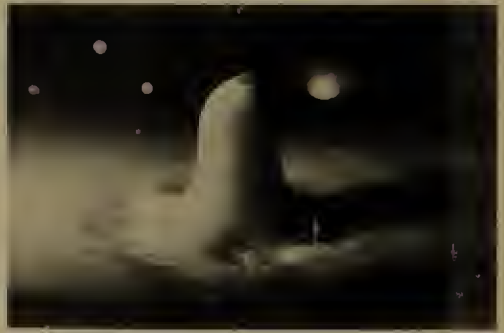
18

t-1319



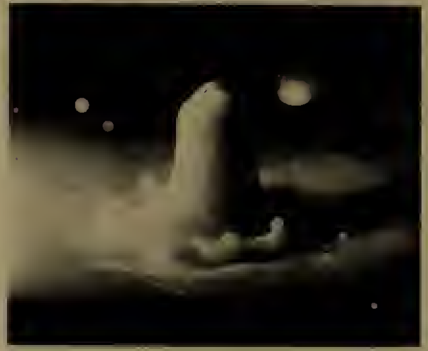
19

t-1492



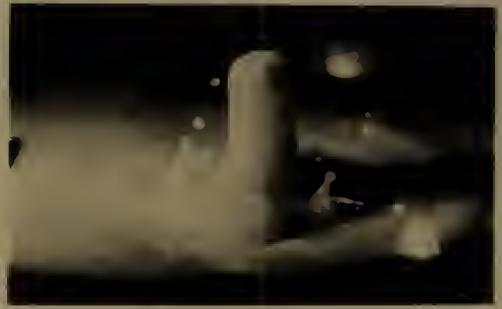
20

t-1610



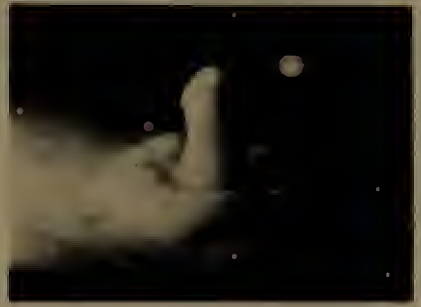
21

t-1694



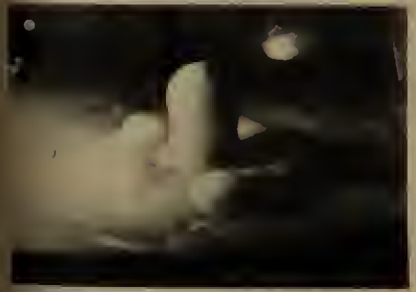
22

t-1938



23

t-1938

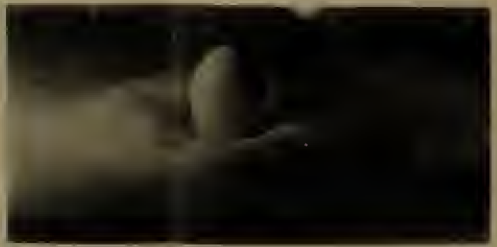


24

t-2093

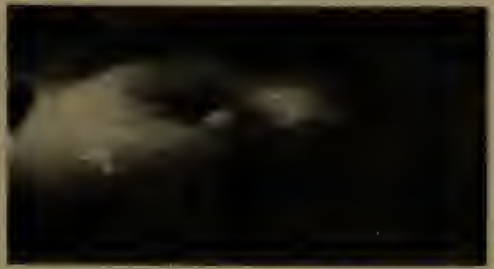
25

t-2173



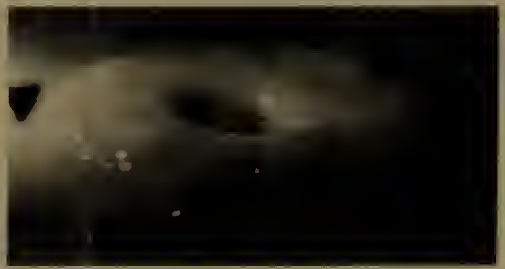
26

t-2400



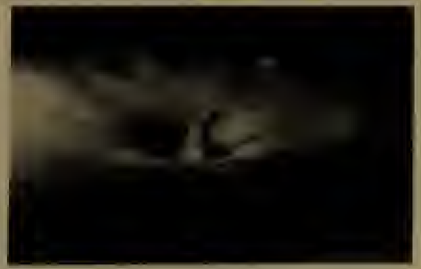
27

t-2718



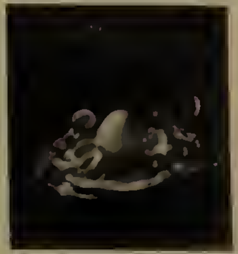
28

t-3106



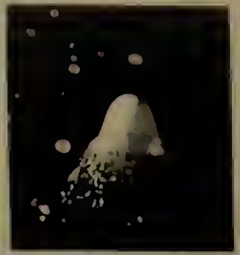
29

t-1025



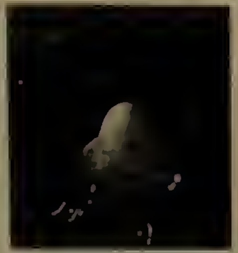
1*a*

t-1106



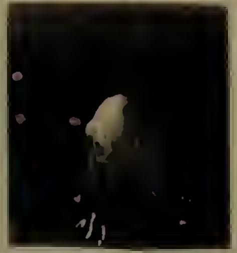
2*a*

t-1182



3*a*

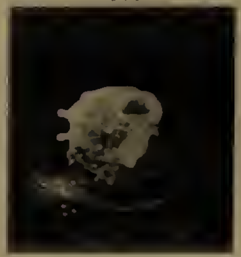
t-1319



4*a*

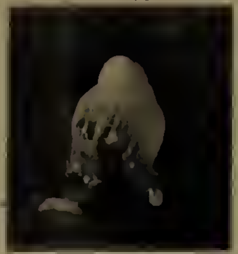
Series II.

t-0950



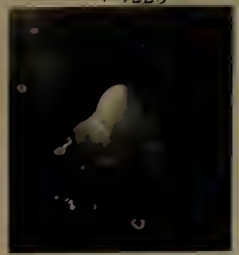
1*b*

t-1134



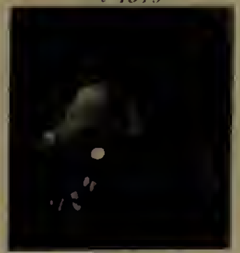
2*b*

t-1228



3*b*

t-1319



4*b*

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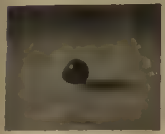
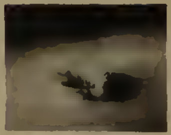
t = 0 (a)



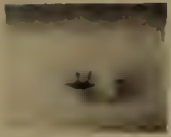
1

t = ·0041 sec. (b)



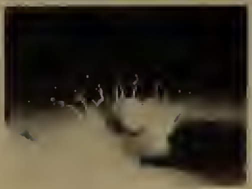
2

t = ·0032 sec. (a)



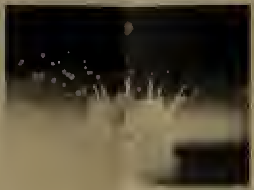
3

t = ·0050 sec. (b)



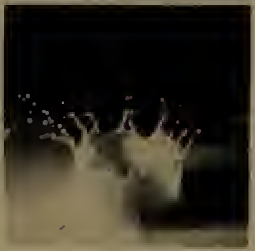
4

t = ·0126 sec. (b)



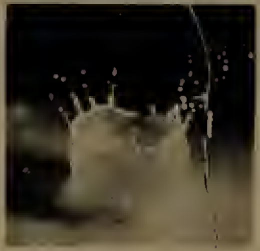
5

t = ·0165 sec. (a)



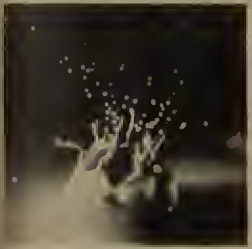
6

t = ·0185 sec. (c)



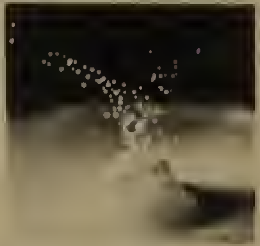
7

t = ·0195 sec. (a)



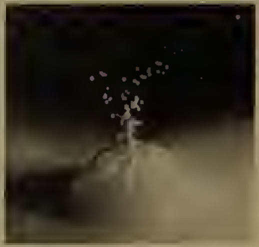
8

t = ·0165 sec. (c)



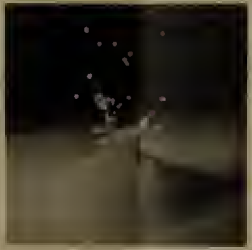
9

t = ·0195 sec. (c)



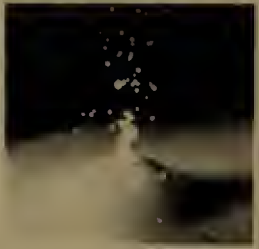
10

t = ·0312 sec. (d)



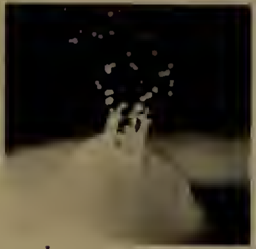
11

t = ·0351 sec. (d)



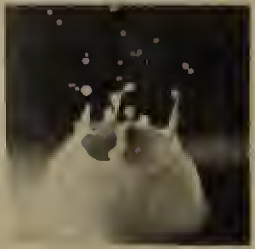
12

t = ·0398 sec. (d)



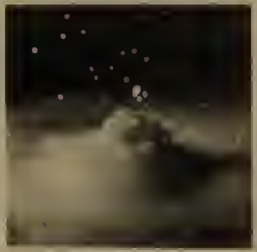
13

t = ·0460 sec. (d)



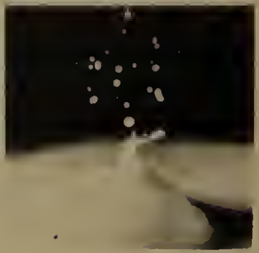
14

t = ·0498 sec. (d)



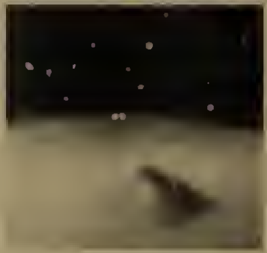
15

t = ·0531 sec. (d)



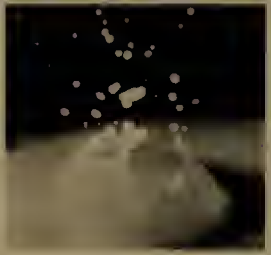
16

t = ·0585 sec. (d)



17

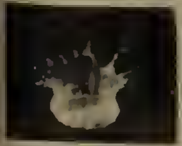
t = ·0704 sec. (d)



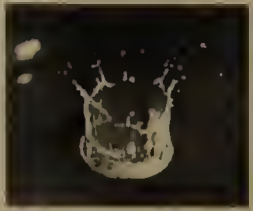
18

Sub-group **A.**

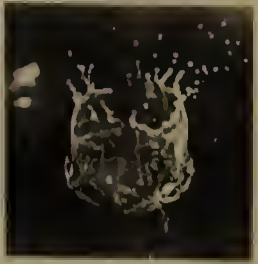
1 (a)



2 (a)

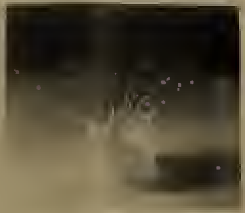


3 (a)

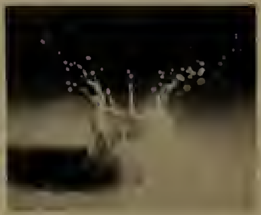


4 (a)

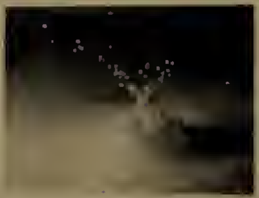
Sub group **B.**



1 (b)



2 (b)

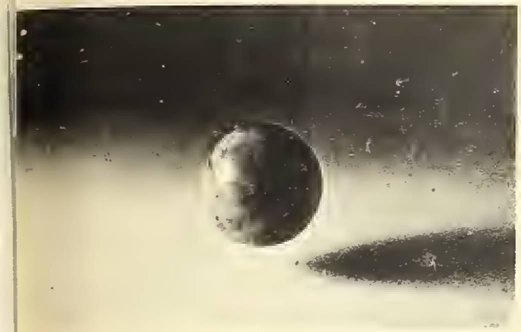


3 (b)

Series III.

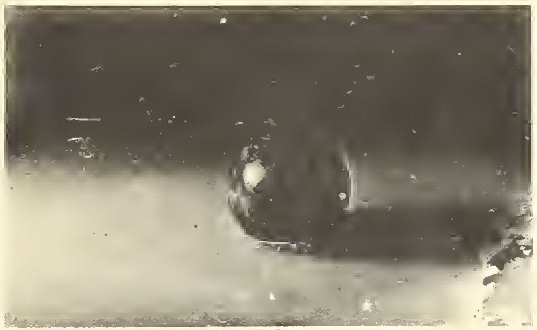
BRITISH MUSEUM
NATURAL HISTORY.

t=0 (*b*)



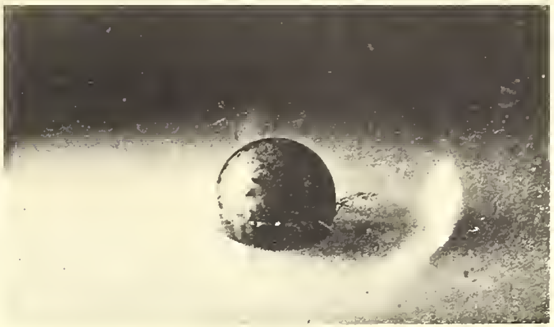
1

t=0 (*a*)



2

t·0028 *sec.* (*c*)



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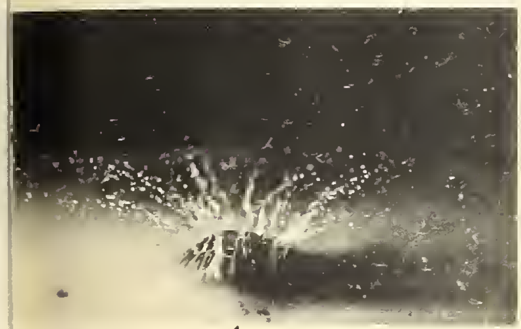

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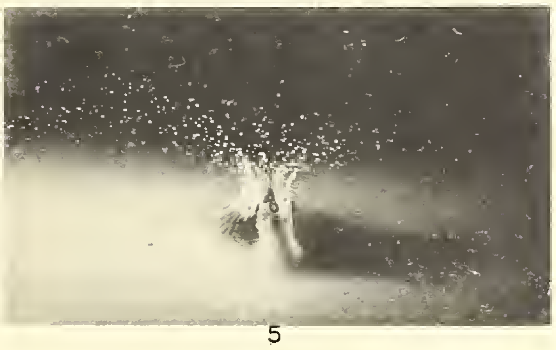

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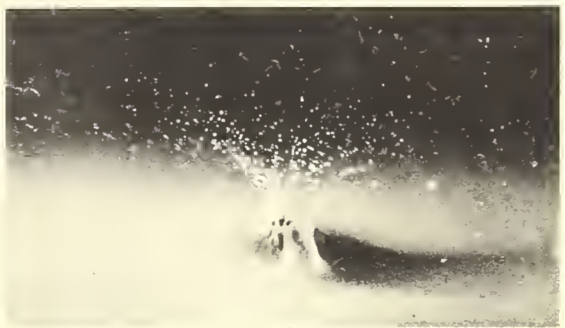

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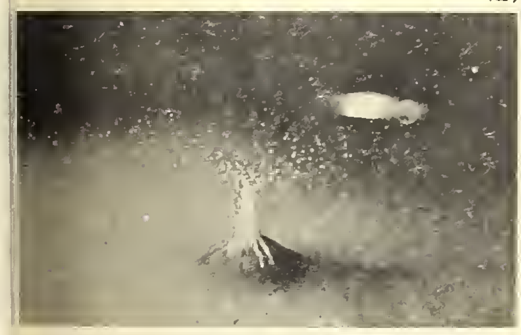

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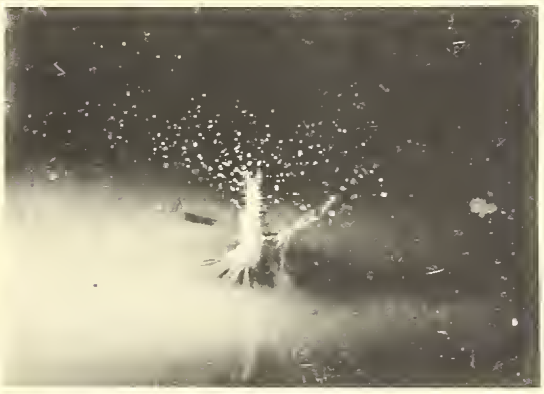

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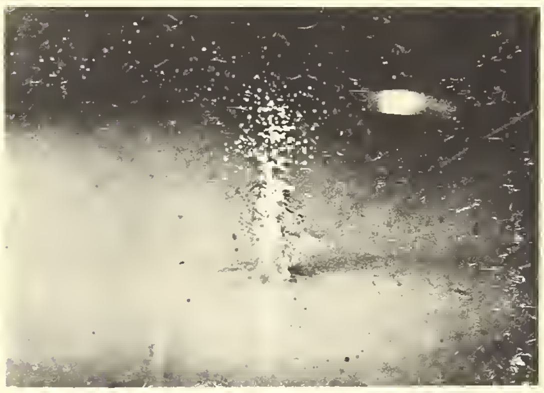

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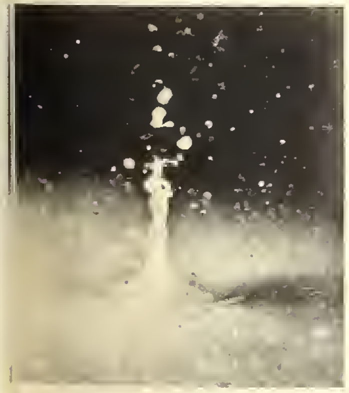
t=·0200 (*e*)



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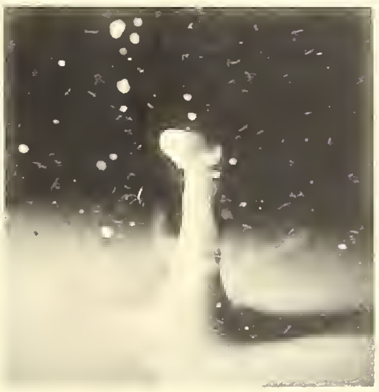

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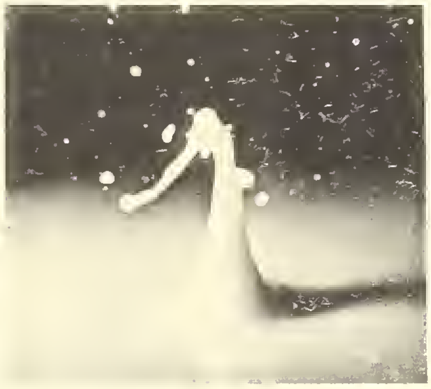

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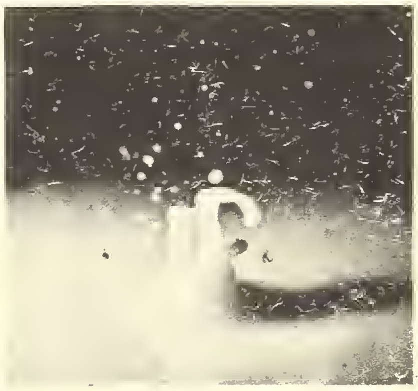

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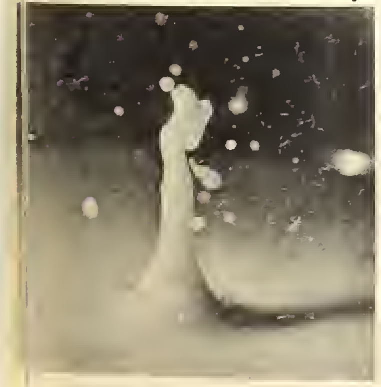

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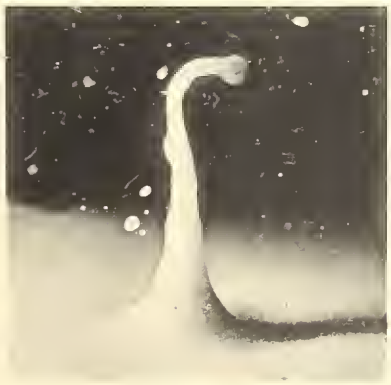
t=·0489 (*e*)



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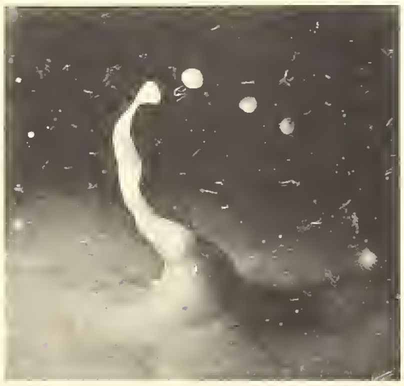
t=·0615 (*e*)



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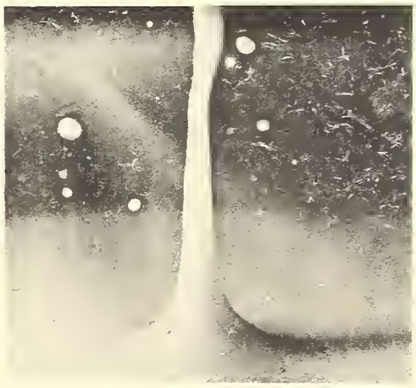
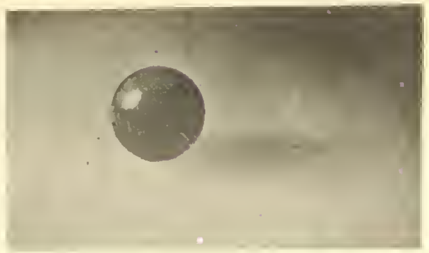


17

Series IV.

BRITISH MUSEUM NATURAL HISTORY.

$t = 0$ (b)



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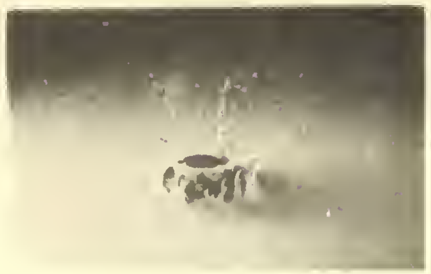

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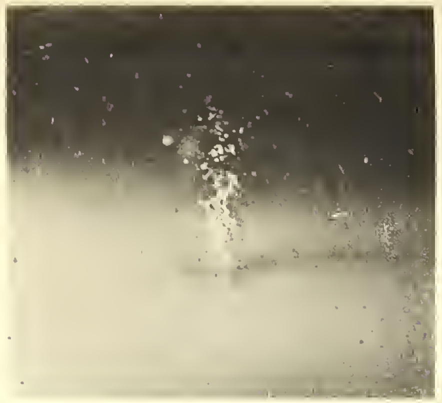
$t = \cdot 0074$ sec. (a)



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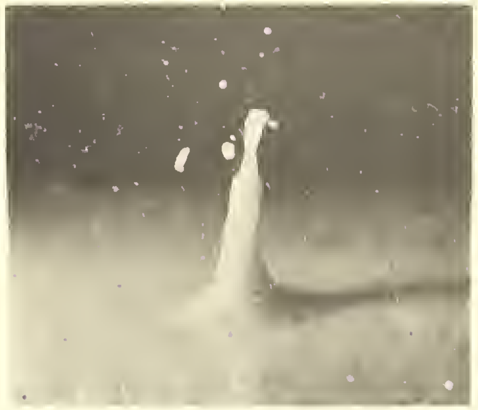

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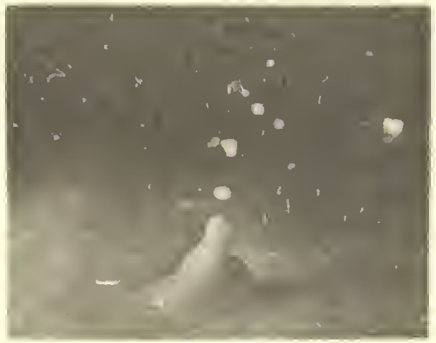

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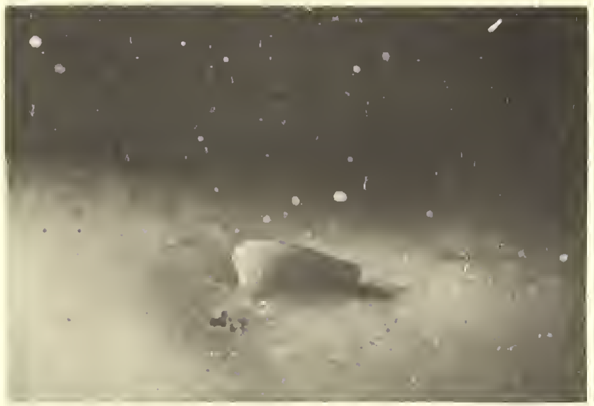

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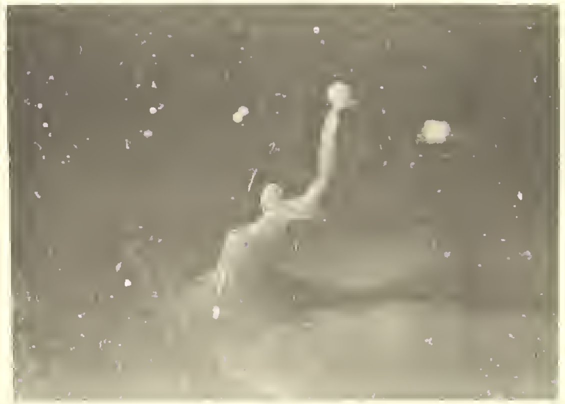

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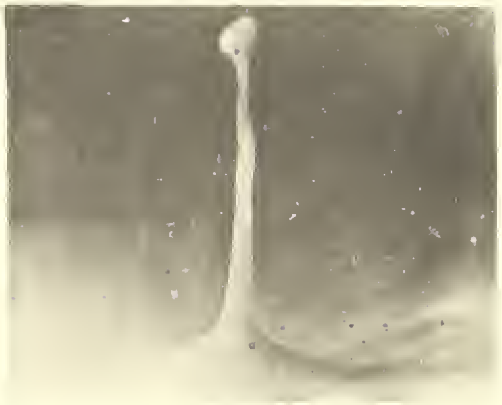

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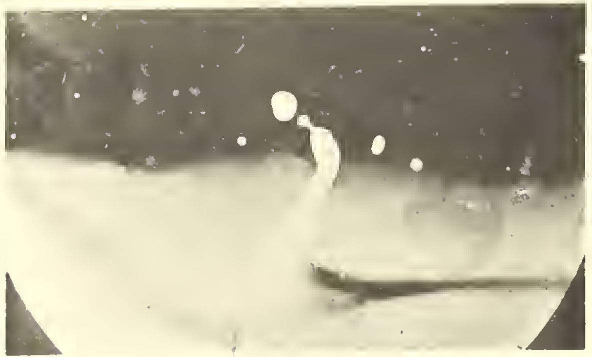

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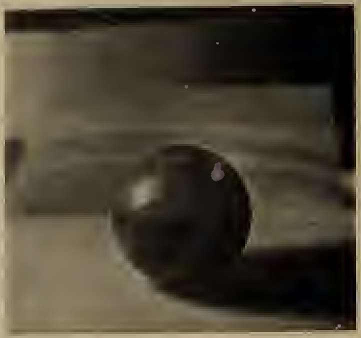
Series V

BRITISH MUSEUM
NATURAL HISTORY



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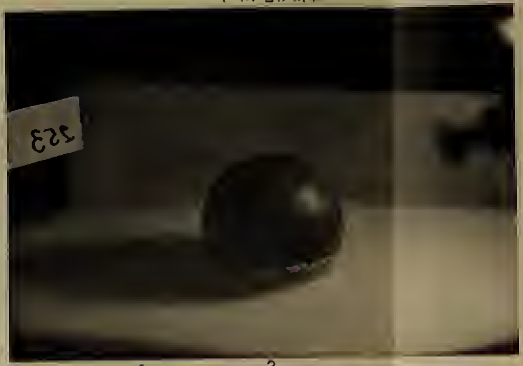

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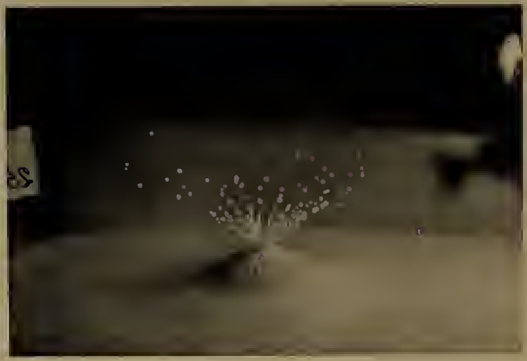

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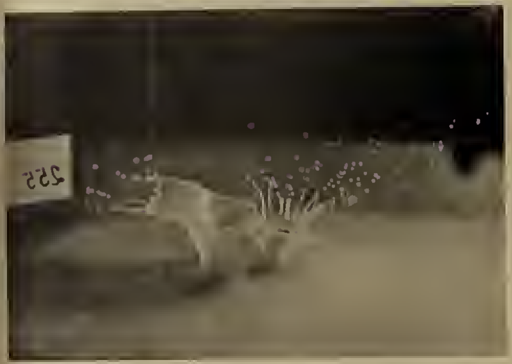

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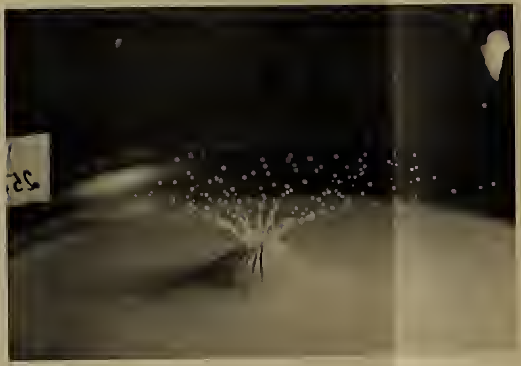

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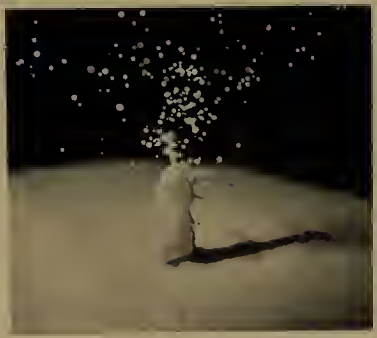

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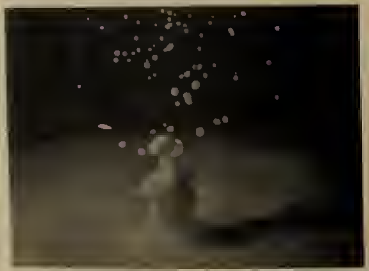

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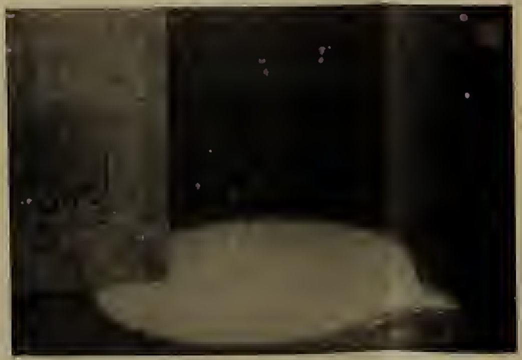

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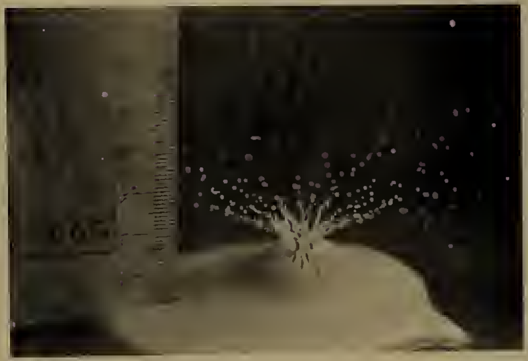

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9

Series VI.

BRITISH MUSEUM NATURAL HISTORY.

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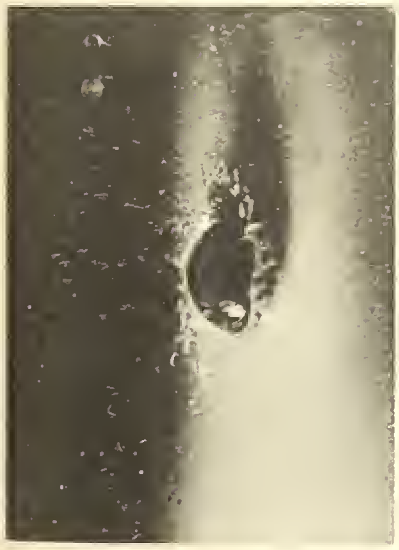

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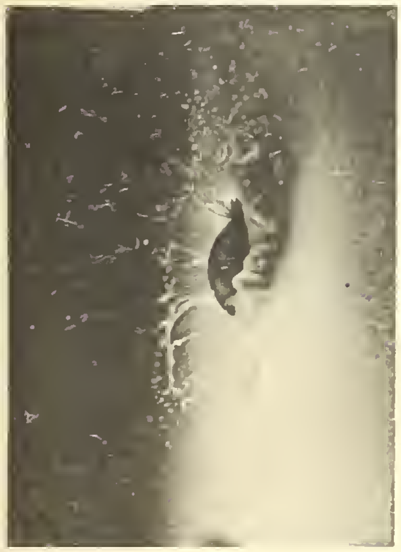

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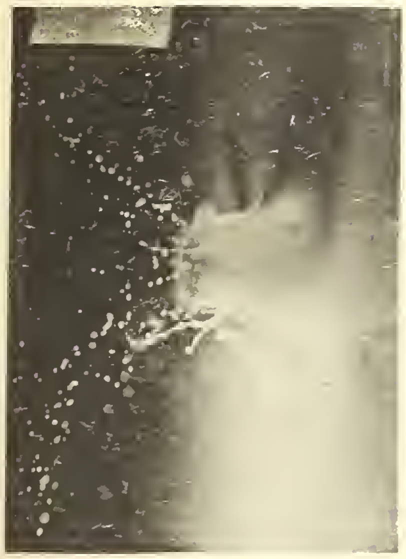

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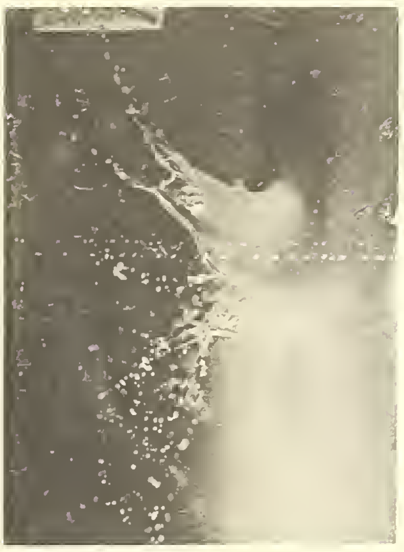

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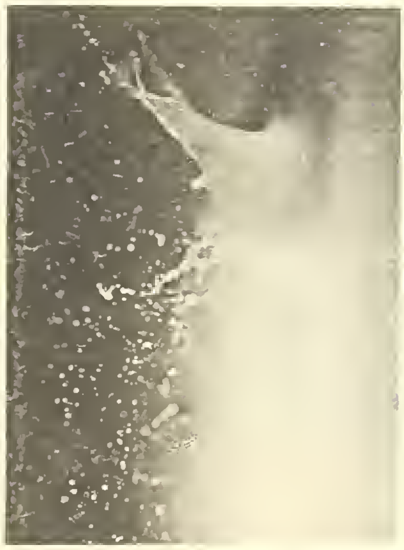

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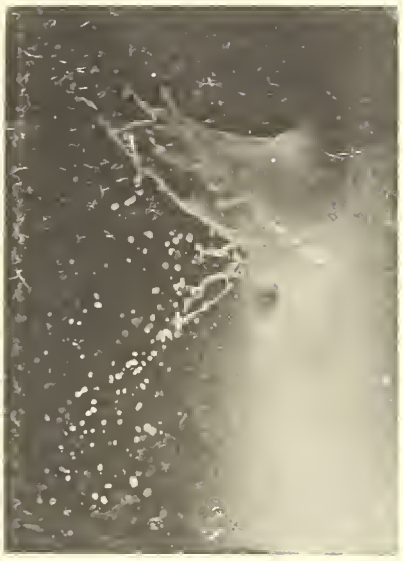

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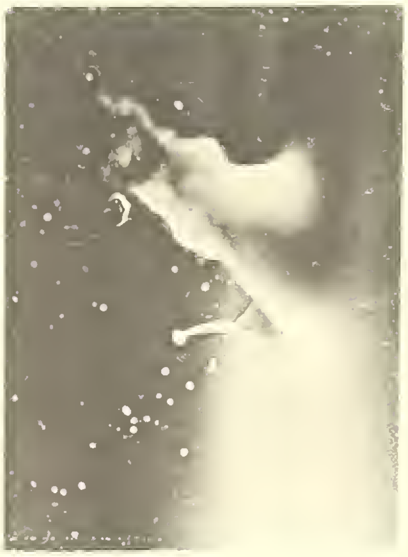

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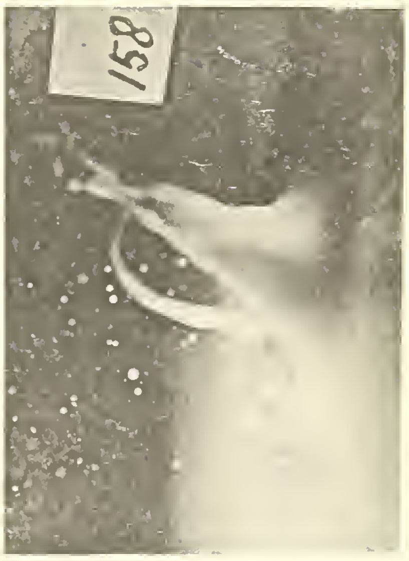
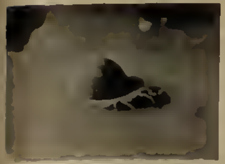


8

Series VII.

BRITISH MUSEUM NATURAL HISTORY

t-0



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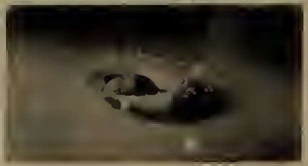

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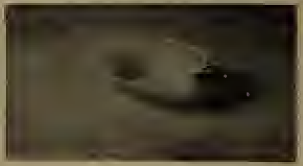

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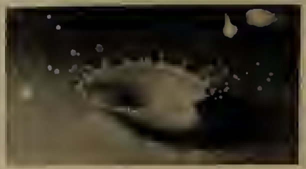

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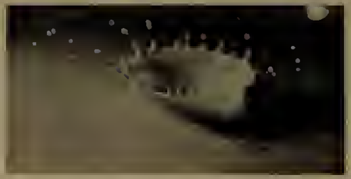

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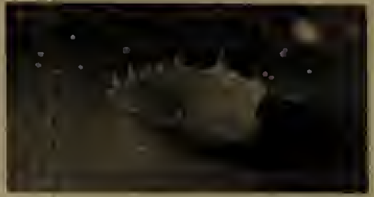

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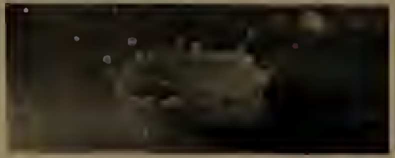
t-0261 sec



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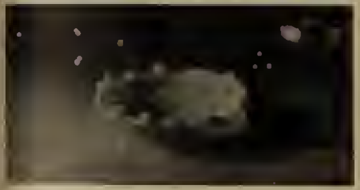

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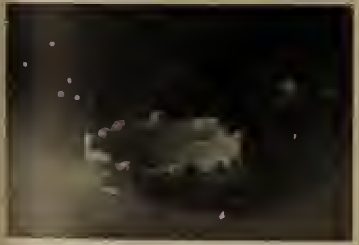

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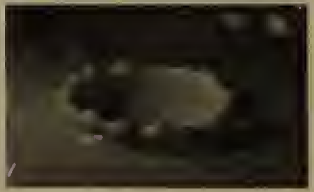

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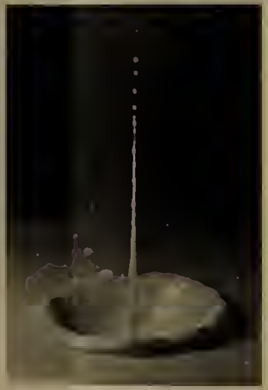

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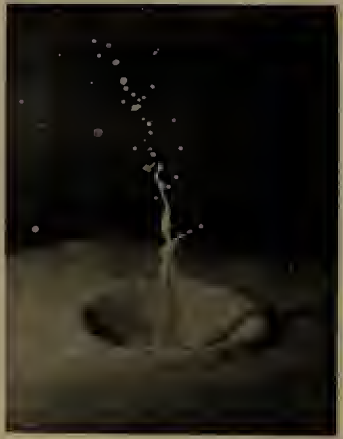

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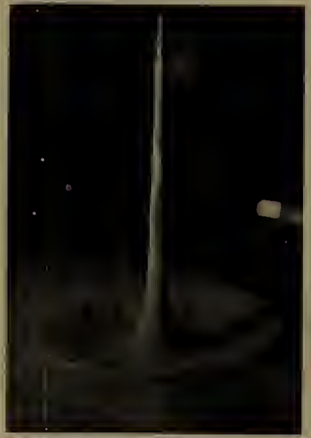

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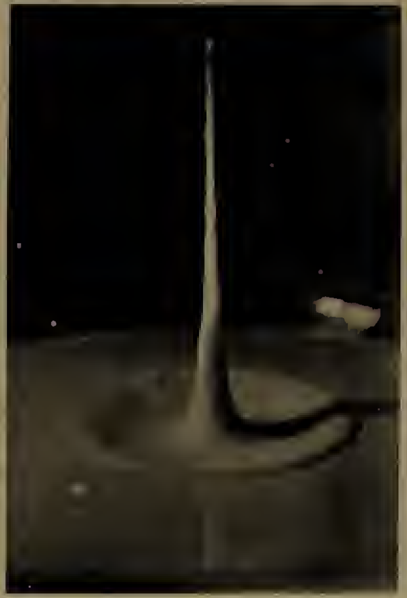

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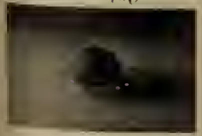
Series VIII.

t-0



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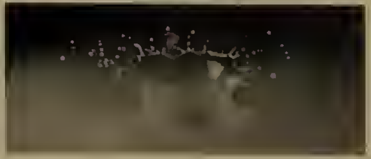

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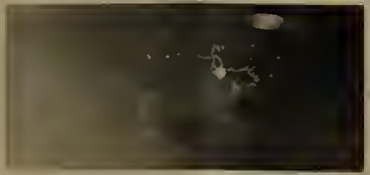
t-006 sec.



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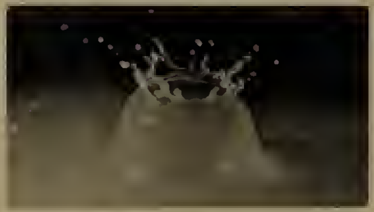

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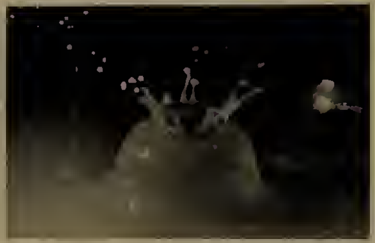

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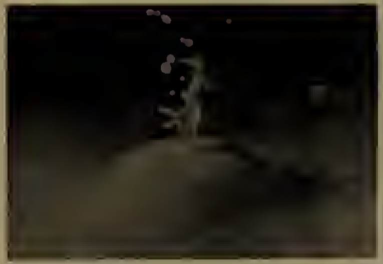

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Series IX.

BRITISH MUSEUM
NATURAL HISTORY.

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VI. *Experiments on the Absence of Mechanical Connexion between Ether and Matter.*

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THE conclusion of the experimental part of a previously published memoir, on "Aberration Problems and the connexion between Ether and gross Matter," dated March, 1892, and published in the 'Phil. Trans.,' Series A, for 1893, p. 777, is as follows:—

"The velocity of light between two steel plates moving together in their own plane, an inch apart, is not increased or diminished by so much as $\frac{1}{200}$th part of their velocity."

Since that date, of March, 1892, a considerable number of further experiments have been made, tending to confirm and extend the above conclusion; and of these experiments it is the object of the present communication to give a brief account. The general plan of experimenting having been sufficiently indicated in the previous memoir, no more details will now be related beyond those necessary to make the record of use to a later student of the subject.† The figures on pp. 759, 761, 767 illustrated the apparatus used.

The chief conclusion of the theoretical part of the former paper (p. 752) is that no first-order effect of purely irrotational etherial motion can ever be optically detected; in other words, that as long as the motion of a medium is characterised everywhere by a single-valued‡ potential function, the course of all observable *rays* through it, however reflected and refracted they may be, is independent of the motion (no matter how the *waves* may be tilted), and the time of journey along any given path through any kind of material is likewise perfectly definite, and independent of the motion, except for experiments directed to the second order of aberration-magnitude.

Hence no attempt to disturb the ether by using a spoked wheel, or revolving bars or paddles, would have a chance of success, unless there existed a trace of something akin to viscosity by which the medium could be got hold of, and as the previous arrangement of apparatus seemed as well calculated as any other to detect the existence of a trace of viscosity, whereby ether in the immediate neighbourhood of moving matter should sooner or later be more or less carried along by it, no fundamental change in the mode of experiment seemed necessary; only improvement in details, and some modifications, in order to secure a closer and a wider generalisation.

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* Assisted by Mr. BENJAMIN DAVIES.

† It may be argued that the details of an experiment having a negative result should not be published; but to me it seems that their publication in that case is more essential than in any other, because on them alone can a judgment be made as to how far the problem has been attacked in a careful and responsible manner, and because an answer "no," *when really attained*, is just as definite and positive a reply to some questions as an answer "yes."

‡ The epithet "single-valued" should be explicitly prefixed to the words "potential function" in § 29, p. 752, of the memoir referred to, 'Phil. Trans.,' A, 1893.

Hitherto the experiments had been conducted with a pair of hard steel disks like circular saws, clamped together on a vertical axis, at a distance apart of one inch.

These disks had been spun, at a speed not exceeding 1250 revolutions a minute in the most accurate experiments, and the effect of the motion on a bifurcated beam of light, whose two halves travelled in opposite directions several times round in the space between the disks, was observed. One half of the light travelled in the same sense as the motion, while the other half travelled in the opposite sense; the two half beams were made to interfere in the field of view of a micrometer eye-piece, and a shift of the central band of the system by so much as the hundredth part of the width of a band could be observed. In making the above careful estimate of the result, however, the safe course was taken of assuming that $\frac{1}{20}$th of a band shift was the minimum certainly detectable.

There were some modifications still to be made before accepting a definitely negative result of experiment.

1st: to steady the motion, so that quantitative readings could be taken without tremor at a much higher speed of rotation.
2nd: to continue the motion for some considerable time, and to narrow the light channel or watch the effect close to a disk.
3rd: to increase the mass of the revolving matter.
4th: to magnetise the revolving material.
5th: to electrify it.

The connexion looked for between ether and matter being something of the nature of viscosity, the space between the disks may be considered rather wide; though it is difficult to suppose that any motion generated at the surface of the disks in a substance possessing any of the properties of an ordinary fluid, should not spread into the nearly enclosed space between them. It may, however, be conceivably argued that this diffusion of motion might take considerable time, and hence the modification labelled No. 2 above was called for. The modification No. 3 is to meet the argument that, even though a viscous connexion between ether and matter were disproved, it did not follow that there was not another mode of connexion competent to transmit motion from one to the other, viz.: the unknown kind of connexion which is concerned in gravitation; and to display any effect on this, a large mass must be used.

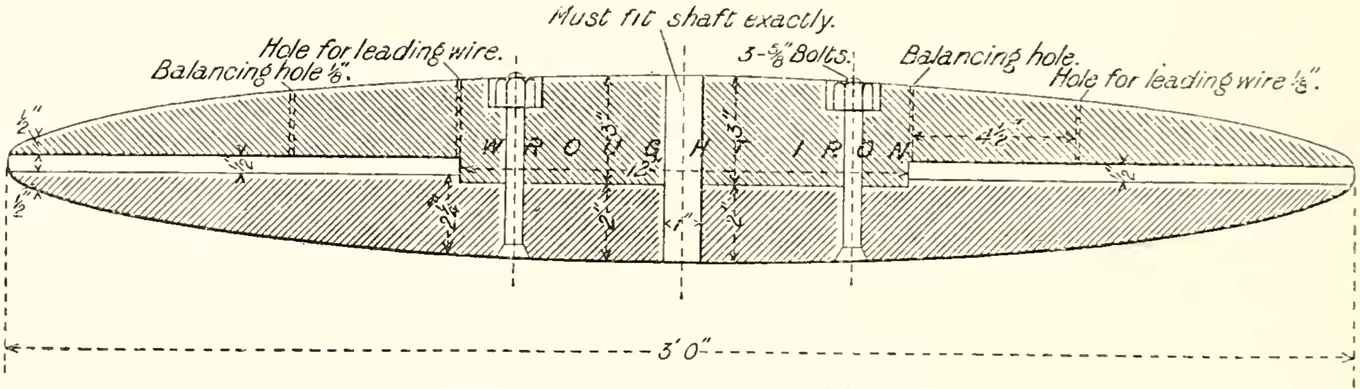
Probably the mass necessary to demonstrate any action of the gravitational kind would be impractically large, unless the earth itself could be used. Now, by staking out mirrors at the corners of a field, it is arithmetically quite possible to arrange for a perceptible shift of the bands due to the rotation of the earth, if it carries ether round with it; but it does not seem possible to experimentally observe that shift, unless some method could be devised of making the observer and his apparatus independent of the rotation.

It is to be observed, that since a motion of the disks relatively to the observer and the light causes no effect, the ether being stationary, it follows that a motion of the light and observer would produce an effect, since they would be moving relatively to the ether. Hence if, instead of spinning only the disks, the whole apparatus, lantern, optical frame, telescope, observer and all were mounted on a turn-table and caused to rotate, a reversible shift of the bands should be seen. It would not matter in the least whether the disks were revolving or not, and they might just as well be absent. The effect would be of an aberrational kind, the opposite light beams being accelerated and retarded by the motion appropriately. In an actual experiment of this kind, centrifugal force would give some trouble by introducing strains, and rapid rotation would be uncomfortable for the observer; but really rapid rotation should be unnecessary to show the effect. My present optical apparatus mounted on a turn-table revolving 4 times a minute should show something, viz.: $\frac{1}{100}$th band shift each way. A certain amount of discomfort during the accelerative stages of any speed could hardly be avoided, and even during steady motion there would be some inconvenience; for instance, at 30 revolutions a minute the observer's weight, at a metre and a half from the centre, would be half as much again, and would be inclined at 45° to the vertical. This, however, might be tolerated.

If the ether is stationary near the earth, that is, if it be neither carried round nor along by that body, then a single interference square, 1 kilometre in the side, would show a shift of rather more than one band width, due to the earth's rotation in these latitudes; see p. 772, 'Phil. Trans.,' 1893. But as the effect depends on the area of the square, a size of frame capable of mechanical inversion is altogether too small; there may, however, be some indirect ingenious way of virtually accomplishing a reversal of rotation—something for instance based on an interchange of source and eye—and if so, it would constitute the easiest plan of examining into the question of terrestrial ether drift.

If matter conceivably drags the ether with it in proportion to its mass, an ordinary lump of matter can hardly be expected to cope with the heart and to shift it in opposition to that body; nevertheless, since nothing is known on the subject one way or the other, it was thought well to give a more massive body a chance, by rotating a solid piece of iron about three-quarters of a ton in weight, and with a much narrower groove or channel cut in it for the passage of the light. It was easy to arrange at the same time for the magnetisation of this piece of iron when desired, so as to be able to attack the question above, numbered 4, without additional expense. Accordingly, I ordered from Messrs. Mather and Platt an oblate spheroid of best Swedish iron, a yard in diameter and half a foot thick, with a deep channel or groove half an inch wide cut into its rim to a depth of one foot all round. It was not found practicable to make the iron all in one piece, and accordingly it was constructed of two pieces bolted together, and its section is shown in fig. 1.

Fig. 1.



Oblate Spheroid for Whirling Machine.

The bottom of the groove was wound with wire to a depth of $4\frac{1}{2}$ inches, the wire used being No. 20 B.W.G. double silk-covered copper; and of it 14 lbs. 10 ozs. was wound on, in 94 layers of 9 convolutions per layer, the central iron core being 1 foot thick. The ends of the wire come out through small holes drilled for the purpose, with balancing holes drilled at equal opposite radii so as to leave the centre of gravity undisturbed, and the wire was then tightly bound with tape and steel to resist centrifugal force.

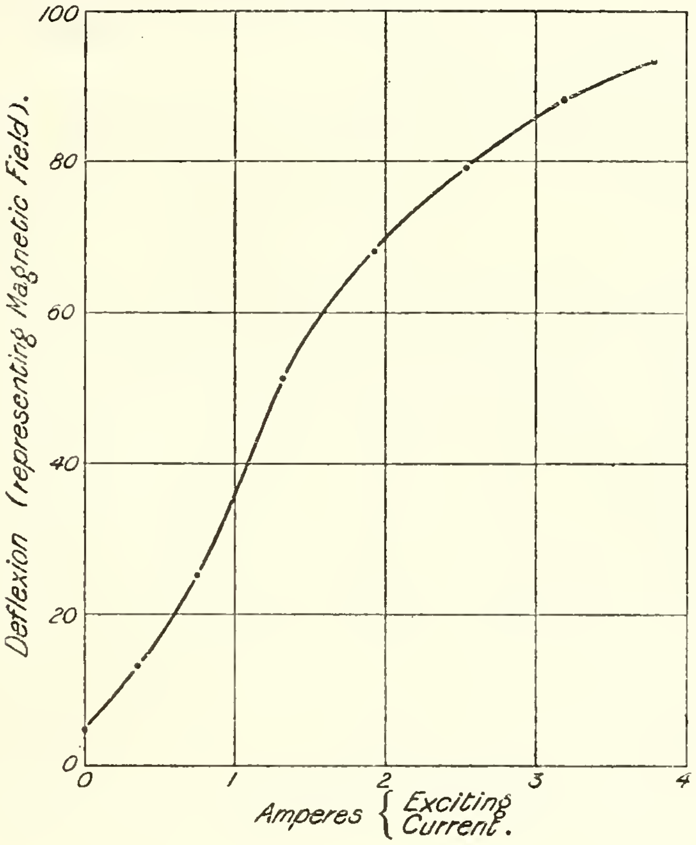
The free ends of the covered wire were clamped to the surface of the disk and led to a set of insulated brass rings on the upper part of the axle, so that an electric current either steady or commutated could conveniently be supplied whenever desired.

The resistance of the wire coil was measured by one of my students as 29·9 ohms, and its insulation resistance was just short of 2 megohms. The length of the wire is about 1 kilometre or two-thirds of a mile.

The magnetising current was usually supplied from the town mains, at 110 volts nominal, which gave a current of 3·8 amperes through the coil of 846 turns, and accordingly developed a magneto-motive force of 4000 cgs.

The lines of force so generated streamed across the half inch gap from the one half of the oblate spheroid to the other, being rather more plentiful in the deep parts of the channel. But the course of the beam of light only partially penetrated into the most intense region, and its mean track was situated about 4·6 inches from the periphery; so at this place I asked a student to measure the magnetic field excited by various strengths of current (by the common method of suddenly snatching out a small exploring coil and comparing the galvanometer throw with that caused by an earth inductor in the same circuit thrown over two right angles). There was a certain amount of permanent magnetism, and the result is indicated in the following table and plotted in a curve (fig. 2). The field intensity was not very different at different depths in the channel; it varied from 1730 cgs. near the rim to 1830 near the winding, when 110 volts were applied.

Fig. 2.



INTENSITY of field in the channel of the oblate spheroid (with decreasing current), at a depth of 4·6 inches from the outside.

Exciting current in amperes . .	0·0	0·34	0·67	1·32	1·92	2·52	3·18	3·80
Field in cgs. lines per sq. centim.	92	255	490	980	1310	1530	1670	1800

The maximum current was commonly used for purposes of excitation; and sometimes for a short time this current was doubled, by the application of 220 volts.

By the 8th June, 1892, this iron mass, weighing 14 cwt., had been mounted on the vertical shaft of the whirling machine, in place of the steel disks, and a spin was taken, with the optical frame in good action, and one half of the beam of light going three times round in the channel of the iron.

The shaft, however, was rather too weak to carry the weight, and exhibited a tendency to bend, which prevented the attainment of high speed. Moreover, the step bearing on which the shaft rested (as described in the previous paper, the shaft was supported on a hard steel pivot resting on another steel surface inside an oil chamber) had insufficient area; the intensity of pressure was too great for lubrication, and accordingly the surfaces ground together and got hot, causing the oil vessel to smoke vigorously. Considerable power was, therefore, needed to drive it, even at 300 revolutions a minute, but at this speed some observations were made. The bands were so clear that $\frac{1}{100}$th of a band shift could have been seen, but there was not a trace of shift when the mass was spinning, either with or without its magnetising current. The 110 volts of the town main were switched on and off and reversed many times, both when the mass was stationary and when it was revolving five times a second, but there was no effect.

Before proceeding to greater speeds it was obvious that the greater part of the weight of the iron mass must be taken off the pivot and dynamo-axle, and must be supported in some other way. A safety collar or guard attached to a frame above the wooden clutch, as shown in Plate 32, 'Phil. Trans.,' A, 1893, suggested the use of ball-bearings resting on this collar, which hitherto had been an inactive safety-guard, but was quite strong enough to support the weight required.

Accordingly we had this arrangement made, all the weight of the spheroid now rested on the guard collar by means of ball-bearings, and the steel pivot had nothing but the dynamo armature to support, this axle also being quite relieved from strain. The old wooden friction clutch was now of course useless, and it was replaced by gripping brass collars on the ends of the joining shafts, just below the ball-bearings, the power being transmitted by a pair of tangential stout copper wires, one on each side, looped round screw heads on the brass collars, so as to transmit a driving couple of considerable magnitude; but if by any accident the force transmitted was too great, the wires could snap and permit independent movement of the mass. Parenthetically it may be here stated that the wires broke several times during the course of the series of experiments, showing that the precaution was very necessary, and that a rigid connexion between the axles would have been dangerous.

During these alterations, other experiments, to be presently recorded, were in progress, and it was not till May, 1893, that careful optical spins were again conducted with the iron spheroid.

At this date the fringes were sometimes used after the light had been four or five times round, but usually the superior brightness and definition of the three-times-round beam was preferred. With a driving current of from 30 to 40 amperes and a voltage of about 80, the speed of 1000 a minute was readily maintained in the heavy mass by aid of the ball-bearings.

At first, however, a new disturbing phenomenon was observed: on beginning a spin the bands began to tremble and became partially obscure. This was not from shaking, nor did it seem likely to be due to wind reaching the semi-transparent plate, because the speed was quite slow. Screens glazed with microscope cover-glass were nevertheless provided, and next day another attempt was made. The flickering of the bands was just the same as before at low speeds, although there was no shaking, but as the speed increased they became clear, and at 800 revolutions were quite sharp. At 1000 revolutions per minute a careful set of observations was made, with the magnetising current applied to the spheroid,—on, off, reverse, off,—many times. But there was no effect whatever on the bands. Then we slackened speed and repeated the magnetisation and reversals down to stoppage, but not a trace of shift. The flickering and blurring of the bands, already spoken of, which still occurred at low speeds, and especially at increasing speeds, was not a serious trouble. It of course prevented exact observation while it occurred, but it was a purely temporary disturbance and did not cause the slightest permanent shift. As soon as the bands were clear again their position was absolutely unchanged. Nevertheless it was desirable to detect and remove the cause of the disturbance. Accordingly air was blown into the channel from foot bellows, but unless the wire coil inside had been recently used and imperceptibly warmed by the current the air jet made very little difference, though if there was the slightest inequality of temperature it caused a slight flicker. But a whiff of coal gas, the merest trace, distorted the bands with agony—sent them waving through ellipses and contortions into invisibility, allowing them to re-appear as the gas diffused away. They were manifestly extremely sensitive to fluctuating density, and hence we traced the previous flicker to hot air from the carbon rheostat which regulated the driving current. It seemed to get drawn into the channel sometimes at low speeds, but at high speeds was blown clear away. Starting and stopping the iron by *hand* did not cause the bands to flicker; they only flickered when the motor was used. It was plainly a heat convection effect. Hence we arranged that the carbon rheostat should be far away, and even the slight heat of the motor itself was screened and diverted off by a suitable platform or tray of wood and cardboard arranged above the motor.

Now I repeated the observations over and over again, with all sorts of changes, and never found either motion or magnetisation of the heavy iron mass cause the slightest real shift of the bands at the speed of 1000.

The channel being narrow, the plates themselves were visible in the eye-piece, and the bands could be seen reflected in them. Also diffraction or interference phenomena could be seen where the bands terminated on the iron (LLOYD's bands due to oblique reflexion) at one or other of the plates. A frequent appearance of the bands under these circumstances is depicted in fig. 3, next page.

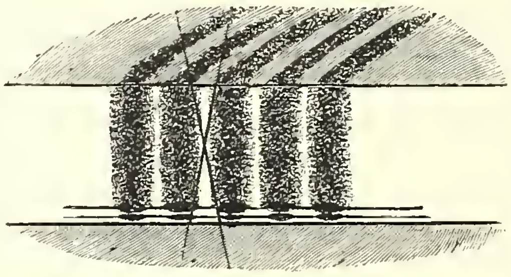
These reflected bands, and also the horizontal boundary stripes with the swellings of the bands on them, were also watched, the cross wires being shifted and set upon one feature after another, but in no case was the slightest shift seen on magnetisation; though certainly the test was not so delicate as with the free-air bands, because the plane of the channel-boundaries was not absolutely steady as the plates revolved.

The bands observed were often so broad that the distance between them was comparable with the half-inch channel-width, and sometimes the cross of the hyperbola-system was used as the feature upon which the cross wires were set, so that an exceedingly small fraction of a band-width could have been observed.

At 1000 revolutions a minute, the ball-bearings began to get hot, and some attention had to be paid to them to get the number of steel shot and the lubrication as perfect as possible. The iron mass took a long time to slow down from full speed, and after being left to itself for twenty minutes or half an hour was still moving. Sometimes it was stopped more quickly by a brake, to see if acceleration had any effect, but none was seen.

On the 8th May, 1893, we had a good spin at 1200 a minute with the spheroid, magnetised and reversed, etc., looking as carefully as possible at the bands reflected in the iron and at every part of the bands, but no change of the minutest kind was visible.

Fig. 3.



Appearance of the interference bands as seen in the half-inch channel of the oblate spheroid. The bands happened to be reflected in the upper iron surface, and to show subordinate interference stripes in the lower iron surface.

On the 9th May, we had a similar spin in the reverse direction, conditions fairly satisfactory, and results definitely negative.

Sometimes an alternating or commutated current was supplied to the coil, but its self-inductance and time-constant were so great that little power could be thus developed. Anyhow, no shift of the bands was seen.

Experiments at Higher Speeds.

During the next few weeks, the iron spheroid was replaced by the old steel disks, and great pains were bestowed on getting these accurately balanced, so that a high speed could be reached without tremor.

By June, the ether machine could be driven at speeds above 3000 a minute, the power used being 50 amperes and 100 volts.

But at these higher speeds there were many difficulties. The blast was, of course, excessively strong, and it was necessary to carefully screen it from the mirrors and frame by boxing the plates up in the wooden drum before described; moreover, higher speeds could be attained with the air thus boxed up. But the air got very hot, and this spoiled the fringes, so that at high speeds they were often invisible. Without the drum the fringes remained visible, but the blast caused a shift often of as much as two bands. This shift came back on stopping, and sometimes rather more than came back, ultimately settling down as if slow strains were working themselves out. The drum was now replaced without floor or roof, and with only very narrow slits for the light to get through. The light was often got four times round. A smaller shift still remained, and there was nothing for it but to glaze the slits, and broaden the drum above and below, so that no trace of air blast could reach the frame, at the same time that there was plenty of ventilation to keep the air quite cool.

It need hardly be said that the presence of so many glass surfaces in the course of the beam increased the difficulty of getting the fringes distinct for the three-times-round path, for each half of the beam had to undergo not only 11 reflexions as usual, before returning to the semi-transparent plate, but also 24 transmissions through panes of glass, *i.e.*, 48 transmissions through a glass-air surface at 45°. The intensity of the beam is thereby greatly enfeebled, and the glass has to be of excellent optical quality and free from strain if good definition is to be got. Ultimately, by selecting from a number of glass plates supplied by Mr. HILGER, the patience of Mr. DAVIES overcame the difficulties, and fringes were got of sufficiently satisfactory quality with the beam three times round; a Brockie-Pell arc light imaged upon the aperture of the collimator, and kept finally steady by hand, being used as the source. It was found that a great width of beam was difficult to use, probably for a reason subsequently to be mentioned (varying air density due to centrifugal force), and a diaphragm was commonly used over the object glass of the collimator.

Under these conditions a set of observations were made, with the speed up to 2,800 a minute, first in one direction, then the other, and then the first way again.

In each case the bands remained visible at the highest speed, though at certain intermediate speeds, especially about 1000 and 1700, a slight tremor smudged them.

The shift observed now was moderately small but quite distinct, and was estimated with the micrometer at $\frac{1}{16}$th band. It repeated itself each time without regard to the direction of spin, and disappeared, though not instantly, when the disks stopped. It seemed probably due to some obscure residual effect of the blast, perhaps on the cover glasses of the drum. The shift was irreversible, and of reversible shift there was none.

At these higher speeds it would naturally be thought that the true theoretical effect due to whirling air $(\mu^2 - 1)$ should be observable; but if its amount be reckoned it will be found to be less than $\frac{1}{200}$th band, and therefore not detectable for certain under the above conditions.

The only effect distinctly due to heat in the above experiments was a flicker of the bands at the lowest speeds, just before stopping. It was due to the gentle warmth of the motor, an air current rising towards the disk and mirrors when the blast was insufficient to drive it away. But it never did the least harm, and could only be seen just before stopping, or sometimes a second or two after stopping. When it was over, the bands were absolutely in the old place; its effect had been to wave them about slowly and slightly.

In all these experiments the brass collar coupling, with the copper wire force-transmitters, was used to connect the two axles, instead of the old friction clutch, which was insufficient and not so dependable.

Possible Time Effect.

On June 6 we kept the disks spinning for three hours at 1900 revolutions, to see if any shift developed with time. The result on this particular occasion was an apparent shift followed by a blur and invisibility of the fringes. They did not recover on stopping, but could be brought into visibility by moving some of the screws. This was evidently a bad experiment, and the apparatus was overhauled and steadied up.

Took another spin next day, at a speed of 2400 revolutions, for three hours, and not the slightest shift developed itself in this time.

By June 23, the step bearing at the bottom of the axle shaft was replaced by a new one, and other mechanical conditions were improved. The machine now ran up to 2400 without a tremor, and a current of 30 to 35 amperes was sufficient to do the driving. An observation was made with the drum in, with glazed windows, no top or bottom (as before), the light going three times round, and the speed being kept at 2100 for two hours. At the first instant there was a shift of $\frac{1}{20}$th band, but it did not increase, nor did it recover on stopping. Went on with a reverse spin, also at 2100, under the same conditions, and saw not a trace of shift at going or stopping, or during long spin—only the usual flicker as the speed got very slow. The bands were distinct all the time. A good experiment. We conclude that time has nothing to do with the matter.

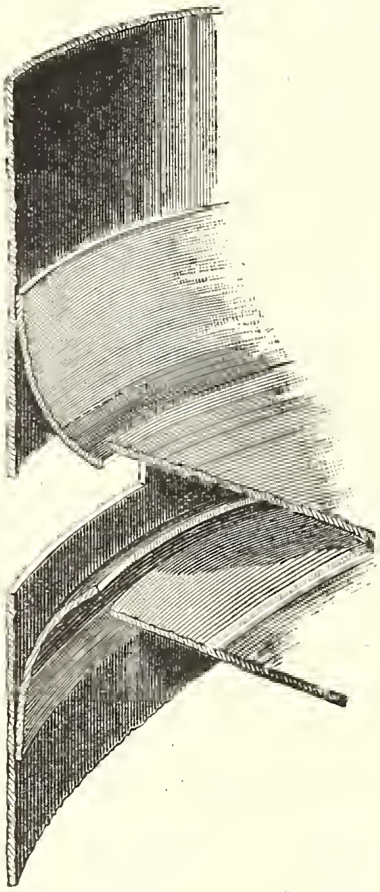
Attempt to Observe the Air Effect.

From June to November, 1893, continual attempts were made (except during a month's vacation), by careful and repeated setting of the micrometer wires on the bands, by taking the average of a set of readings at each speed and plotting them, to get some dependable record of the true air effect, free from disturbing causes. This labour was undertaken not only because it was thought of interest to observe this hitherto unobserved small quantity, but also because its detection would emphasise the truly negative character of the ether effect.

Taking μ for air as 1·00029, the $k = 1 - \frac{1}{\mu^2} = \cdot 00058\ \theta$, and the fraction of a band shift observed being x at an angular speed ω, and with n light-journeys round the optical square of side a, we should have $kn\omega a^2 = 4 \times 10^5 x$ (see p. 772, *loc. cit.*); wherefore, writing $\omega = 2\pi N$, and considering that the observable x is $\frac{1}{100}$th of a band, it follows nN must be 300, in order to show the air effect, that is, the speed must rise to 6000 revolutions a minute with a light-journey of three times round. This speed would lead impractically near to the bursting-strength of materials; but it was hoped that, by taking the average of a series of settings, $\frac{1}{200}$th of a band could be safely observed, and thus the effect of the air-spin detected. And if everything had gone well, I think this might have been done, but the difficulties met with caused a careful examination of the brick pillars and foundations beneath the floor, with the result of discovering that the brick pillars, by which the optical frame was ultimately supported on its gallows support (fig. 11, p. 767, 'Phil. Trans.,' 1893), were not so entirely independent of the whirling machine's stone altar as they ought to have been. During the vacation bricklayers and carpenters were accordingly called in to re-set the warped pillars beneath the floor, and to clear away all joists and everything that could be suspected of in any way helping to transmit vibration. The result of this work was a beautiful steadiness and visibility at high speeds; but still the bands showed what we call a concertina action, that is, a slight moving of the lateral bands in or out from the central one, as the speed varied. There would be no strong objection to such motion, if the precise symmetry of the central band could be assured, but, as this assurance was not forthcoming, the central band sometimes shared in this motion; and even if it did not, its steadiness was suspicious, because perhaps it *ought* to have slightly moved.

The residual trouble appeared possibly due to an obscure influence on the glass windows of the drum, possibly a slight warping due to warmth or air pressure, and an attempt was made to dispense with the window panes and to screen from the blast by another method. Accordingly a fresh drum was made of brass, with a pair of deflecting rims or flanges, so placed as to catch the air whirled off the disks all round, and deflect it out of the way upwards and downwards, the light passing on through a chink or slit in the brass drum to the region protected by these flanges (fig. 4).

Fig. 4.



Some residual draught did however manage to reach the mirrors, and, although they were strongly supported, it seemed to flutter them even if unable regularly to tilt them. It was then attempted to lessen the freedom of air supply to the axis of rotation, by wooden circular boards, fitting the axle loosely, and nearly as large as the drum, thus greatly interfering with the supply of air. As soon however as the ventilation was thus interfered with the air got distinctly hot, which was a worse evil.

The drum was supported separately on long wooden girders, so that no part of it was in immediate contact with the optical frame. The girders at first rested on the same gallows as supported the frame (as shown in the figure, page 767, just referred to), but this was ultimately found to be bad, because of a torque received from the whirling air and transmitted to these piers, which conveyed some trace of it to the frame. So while the frame was still supported on its independent piers, and the whirling machine was still clamped to its massive stone altar on the rock, the drum which received and screened the blast was now separately supported by special uprights from the floor (on which people did not walk during an observation), and this, on the whole, was an improvement. Any torque effect, however minute, being of a reversible character, was peculiarly dangerous, for it might easily have been mistaken for a result of the kind that was being looked for.

This memoir shall be abbreviated by the omission of all the careful sets of readings taken during this period, a record which occupies seventy pages of the laboratory note book; for it must be admitted that, although representing a good deal of work, they fail ultimately to show the air effect; and this probably for the reason that any effect of that magnitude would be certainly masked by the residual slight disturbing causes present.

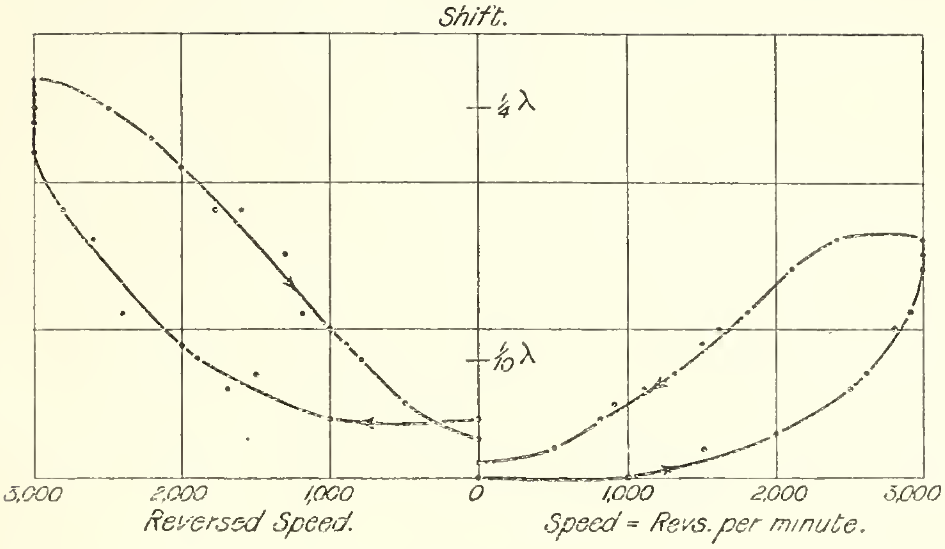
The only thing I will record is a plotting of one of the larger spurious shifts (obtained before the foundation was inspected and altered) to illustrate its typical lagging character. The dots in this case represent individual readings, not averages of setting, and they incidentally show the kind of setting which is possible at high speeds through all the cover-glasses, with the light three times round, and when the steadiness was by no means perfect. The process was as follows:—

The micrometer wires were set, the single vertical wire in the middle of the middle band, and the X wire on the yellow of the first band to the left; or else *vice versâ*. Both wires were read, at gradually increasing, and then at decreasing speeds, and the results plotted on the right-hand side of the two diagrams (figs. 5 and 6), so as to show (*a*) the shift of the middle band due to strains and slight communicated tremors, (*b*) the change in the scale of wave-length due to concertina action. Then the brushes of the dynamo were reversed, and another spin taken in the opposite direction, and then the readings taken which are plotted on the left-hand side of the two diagrams. The total maximum shift was about $\frac{1}{4}$th of a band on this occasion.

The following *averages* of a set of readings taken in July, 1893, may also be quoted:—

With disks stationary, the middle band read . .	94·4	each division being	$\frac{1}{61}$th	of a wave-length.
Disks revolving 3000 a minute, the middle band read	94·4	,,	$\frac{1}{59}$th	,,
Disks stationary again, the middle band read .	95·6	,,	$\frac{1}{67}$th	,,
Disks revolving 3000 a minute in the opposite direction, the middle band read	95·5	,,	$\frac{1}{77}$th	,,
Disks stationary again, the middle band read	92·3	,,	$\frac{1}{60}$th	,,

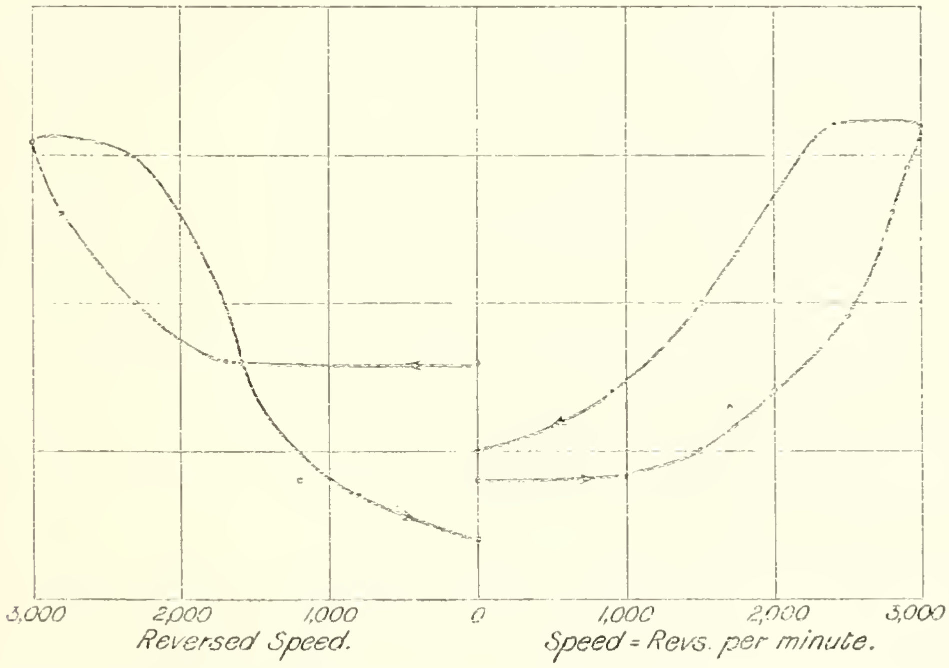
Fig. 5.



Details of one of the larger spurious shifts of the middle band, as observed before the brick pier supports of the optical frame had been properly overhauled.

The dots represent individual settings and readings of the micrometer cross wire set on the middle band during a pair of spins in opposite directions, while the speed was first increasing and then decreasing.

Fig. 6.



Corresponding concertina action (on same scale), or change in the breadth of the bands during the above spurious shift. Dots represent differences between the readings of a micrometer wire set on the yellow of the 1st order and the readings of the cross wire set on the middle band. The zero of the vertical scale is far below, 7 squares below 0. At that distance this figure may be placed above fig. 5.

(To realize that such readings fail to show the air effect it may be simplest to write down ideal readings that *would* show it exactly, viz. :—

94·4 each division being $\frac{1}{60}$th λ
94·1 ,, ,,
94·4 ,, ,,
94·7 ,, ,,
94·4 ,, ,,

if they had been obtained.

Or the following would do equally well, though less obviously :—

94·4
94·6
94·4
95·2
94·4

where there is an irreversible shift of half a division ($\frac{1}{120}$ λ) superposed upon the reversible effect.)

After the overhauling of the foundations, in September, the bands were beautifully distinct, and there was no tremor. There was now no clearly perceptible shift of the middle band, but still there was a concertina action, shown by a broadening of the bands during spin, thus altering the scale of wave-length. The following extract will serve to illustrate this :—

8th September.

With the Disks at rest, the middle band read	7	while the yellow of the first band read	85	divisions.
With the Disks spinning 3000 revs., the middle band read	7	,, ,,	107	,,
With the Disks at rest, the middle band read	7	,, ,,	85	,,
With the motion reversed 3000 revs., the middle band read	7	,, ,,	102	,,
With the Disks at rest, the middle band read	7	,, ,,	85	

Here the constancy of the number 7 means that no change could be seen, but the readings are not averages, nor was the wire reset, and nothing less than a whole division shift would have been observed. The air effect would require $\frac{1}{2}$ a division shift. The existence of the concertina effect was held to render useless an attempt to take a serious set of averages; and by no means could it be wholly got rid of.

Ultimately we decided to do away with the optical frame so close to the disks altogether, and to arrange the mirrors at a distance, out of the blast, on brackets fixed to opposite walls of the room, sending the light round a large oblong instead of a square, and letting two sides of this oblong pass through the channel between the disks. (The arrangement of this experiment is shown in fig. 8.) Meanwhile, we dismantled the machine and sent the disks back to MATHER & PLATT to be fitted with a third one for electrification. (26th Oct. 1893.)

If there were good reason to push the experiment still further (and for the present I see no such good reason), I should be disposed to attempt placing the disks in an air-tight chamber, kept exhausted by a mechanical oil pump, so as to do away with the greatest part of the troublesome air phenomena.

A possible reason for the concertina effect, and for the slight residual irreversible shift sometimes observed, suggests itself in the gradation of density in the air between the disks, due to centrifugal force. To estimate its magnitude under any circumstances, we may consider the equilibrium of an element dm of air at radius r and write :—

$$r\omega^2\,dm = \frac{dp}{dr}\,dr\,.\,rd\theta,$$

or

$$\rho r\omega^2\,dr = dp = kd\rho,$$

whence the density at any radius is

$$\rho = \rho_0 e^{-\frac{\omega^2}{2k}(a^2 - r^2)}\,.$$

Hence, for disks a yard in diameter making 3000 revolutions a minute, the density at centre is about $\frac{8}{9}$ths of that at circumference; and the change of density per centimetre breadth of beam, at a radius of 1 foot, is

$$\frac{dp}{dr} = {\cdot}425 \times 10^{-5};$$

which, if $\mu - 1$ be taken as proportional to ρ, gives $d\mu$ about equal to $\cdot 23 d\rho$; or say 10^{-6} as the difference of refractive index, on either side of a beam of light 1 centimetre broad, in the region of the mean light path. This is equivalent to the effect of a difference of temperature, in the air on either side of the beam, of a $\frac{1}{5}$th of a degree centigrade.

The gradation of density could therefore cause a distinct effect if the beam of light had an odd number of paths between the disks; but since there are in our case an odd number of reflexions, and therefore an even number of paths, with the beam laterally inverted at each reflexion, the effects must very nearly compensate each other.

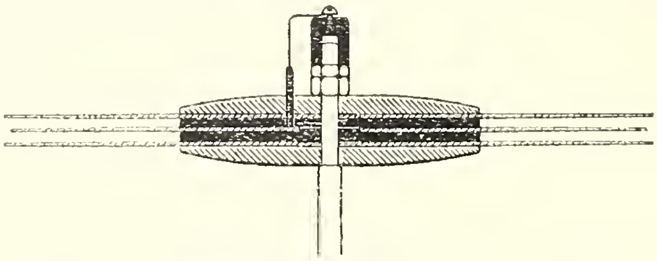
If by reason of some want of symmetry there was on the whole a centimetre length of path uncompensated by a laterally inverted portion elsewhere, the corresponding retardation due to gradation of density would be a millionth of a centimetre, causing an irreversible shift of $\frac{1}{50}$th of a band. This cause may therefore account for part of the residual irreversible shift observable at high speeds, when all kinds of mechanical and thermal disturbance have been apparently eliminated.

The question of Electrification.

Although it must now be taken that such masses of matter as we had been dealing with are incompetent to disturb the ether in a rotational manner (for, as has been emphasised in the previous memoir, irrotational motion of a single-valued kind could not be detected by interference or any other optical experiments, since such motion in no way affects either the path or the speed of a ray), and although further it has now been shown that the conveyance of a magnetic field by moving matter confers no power of gripping the ether, yet it was thought possible that electrification might do it; because an oscillatory charge certainly radiates wave motion into the ether. And although radiation is not any known kind of mechanical disturbance, but is concerned with the ether's electrical properties, and need not necessarily involve anything analogous to etherial viscosity even in the neighbourhood of matter, yet it was thought possible that electric charge, being as it were the connexion between ether and matter, might confer upon a material body some power of gripping and rotationally carrying forward the ether in a quasi-viscous manner. At any rate, whatever reason could be urged for or against such a connexion, it was desirable to bring it to the test of experiment and superpose an electric field upon the moving disks.

The natural plan for electrifying the disks would seem to be to make one of the disks positive and the other negative, but after consideration it was found impracticable to insulate the existing disks satisfactorily; and a third disk half way between the other two was contemplated. This might possibly have been stationary and independently supported, but some preliminary experiments with a plate thus held showed that in the draught of air it developed some warmth and interfered with the fringes; so a rotating disk, clamped in insulating washers between the other two, was decided on, and made as shown in fig. 7. The new disk was made an inch smaller in diameter than the others, but otherwise it was just like them. Connexions were arranged through insulating holes for the supply of electricity near the axle

Fig. 7.

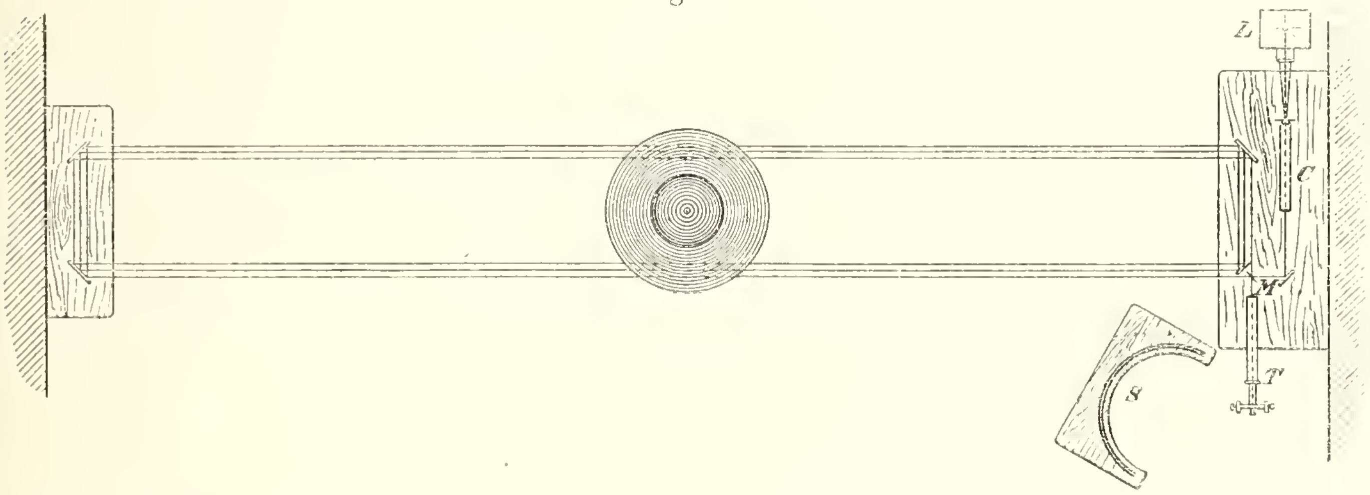


Arrangement of the insulated steel disk between the other two, showing the mode of electrical connexion, with an axial stud touching a Voss machine terminal.

while spinning, and with a Voss or Wimshurst machine a constant succession of sparks could be maintained from the middle insulated disk to the earthed outer ones. These sparks were about half an inch long, and were sharp and clear: they usually occurred from its rounded edge, but sometimes from its flat surface, which on account of the bevel was slightly nearer the other plates than the edge was. It may be taken that the difference of potential concerned was not far short of 40,000 volts., and that the electric tension was about as much as common air can stand.

The interference bands could now be seen bisected by the middle disk, and usually either the upper or the lower half was used for an observation, the positions of the bands close to one of the plates being specially watched, especially at and before each spark, while the disks were revolving at 2800 a minute and the light going three times round.

Fig. 8.



One of the latest arrangements of the optical parts, on the opposite walls of a room, so as to be undisturbed by the force or heat of the blast from the disks revolving in the middle of the room. L is the electric lamp; C, the collimator; T, the double micrometer telescope; and S the double boiler-plate screen to protect the observer; M is the semi-transparent plate, and the light is indicated going three times round a rectangle, with part of its course between the disks. The whole is drawn to scale, the diameter of disks being 3 feet, or nearly 1 metre.

The experiments were chiefly done in February, 1894, and the bands were broad and clear. There was a trace of irreversible shift when the disks were spinning, but its amount was quite independent of the direction of rotation, and there was not the slightest difference whether the plates were electrified or not.

The path of light in this set of experiments was the long oblong with two of its sides between the disks as already briefly mentioned. The mirrors were supported on opposite walls of the room, and a diagram of the arrangement is annexed (fig. 8), the light being sent three or more times round the oblong.

With this plan, *alternate* light paths go between the disks, and accordingly the density-gradient-effect, if any, is uncompensated. A very narrow beam was used, however, and the effect is demonstrably small, though it probably accounts for the irreversible shift observed.

There was not a wink when the sparks occurred, whatever the speed. The test for electrification effect is easy, because the charge can be switched on and off while in a state of steady spin, and the slightest difference would be observed. There is certainly no perceptible effect.

When the disks were slowed down and nearly stopped, there was the old temporary flickering of the bands, but this had nothing to do with electrification, it was merely irregular warmth in the air.

We tried also a couple of Leyden jars with their outer coats connected to the disks, so as to get strong "B" sparks between them (see 'Proc. Roy. Soc.,' 1892, vol. 50, pp. 4 and 18), but still there was no effect.

Without further delay I conclude that neither an electric nor a magnetic transverse field confers viscosity upon the ether, nor enables moving matter to grip and move it rotationally.

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VII. *An Attempt to Determine the Adiabatic Relations of Ethyl Oxide.*

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Received November 6,—Read December 10, 1896.

THE object of the research described in this Memoir is the determination of the behaviour of ether, in the state of gas, approaching towards the state of liquid, when no heat is communicated to it, so that its condition is altered adiabatically. Some experiments have also been made on liquid ether, an account of which we append. After several proposals, depending for their success on the sudden expansion of the substance, so that it might cool without sensible entrance of heat, recourse was had to a modification of KUNDT'S process, whereby the velocity of sound in the liquid or gas is ascertained. The material for research, pure ether, was prepared and dried as already described in a paper by Dr. YOUNG and one of the authors ('Phil. Trans.,' A, 1887, p. 57, *et seq.*). It had a constant boiling-point, identical with that already given.

The experiments were carried out by EDGAR PERMAN and WILLIAM RAMSAY during the Session 1891–1892. Various attempts were made to deduce from the results, by a graphical method, the true position of the curves representing the adiabatic expansion of the gaseous ether, but with small success. At a later date, J. ROSE-INNES examined the figures contained in the tables annexed, and making use of the fact that, without serious error, the isochoric lines, as in the case of isothermal expansion, may be regarded as straight, contributed the mathematical treatment given in Section 5.

For want of sufficient knowledge of the thermal data for liquid ether, a similar treatment has not been found possible; but it is the opinion of the authors that the experimental data should be published, inasmuch as they may be found in future to afford a means of determining the adiabatic relations of a liquid, of which the behaviour in the state of gas is now obvious.

I. APPARATUS EMPLOYED.

The pressure apparatus, A, was the same as that employed in the former research, but important modifications had to be made, so as to render it fit for its present purpose.

31.5.97

between 100° and 130°; bromobenzene, giving a range of 130° to 150°; aniline, of 160° to 180°; and quinoline, of 180° to 200°. Observations were always made at even temperatures, the pressures being adjusted so as to cause the liquid to give off vapour of the temperature required—100°, 110°, 120°, &c., up to 200°.

The method of filling the tube also requires description. First, as regards the powder introduced to show the wave-lengths of the vibrating gas. In air and similar gases, lycopodium dust gives the most distinct figures; but it is a resinous substance, and hence it was not possible to place it in contact with ether. After many trials of magnesia, alumina, precipitated silica, &c., a quantity of somewhat impure silica was prepared, by fusing glass with carbonate of sodium and potassium, and treatment with hydrochloric acid; this gelatinous silica was not very well washed, but was dried in a somewhat impure state, containing a trace of common salt. It was ignited, and fritted together to rough lumps. These were powdered in an agate mortar, and sifted through gauze. The small fragments of microscopic size were approximately spherical, and flowed easily, not adhering to each other. Pure silica is too dusty; sand is too large-grained, or, if powdered, too angular; to obtain the best results the grains should be round and not too small.

A sufficient quantity of such sand was introduced into the experimental tube; its open end, A (fig. 3), was then sealed to a bulb, B, of the form shown in the woodcut; and the tube at the seal was drawn out into a wide capillary, C. Ether was placed in the bulb, and the open end, D, was then connected with a water-pump, and the bulb was exhausted. The ether began to boil and expelled air from the bulb. By admitting air, ether entered the experimental tube, A; and the bulb was again exhausted and then sealed at E. The amount of air was then reduced to that dissolved in the liquid ether. The experimental tube was next warmed, so as to boil the ether it contained; the vapour rushed up, driving pistons of liquid before it, and condensed in the bulb, which was artificially cooled. After about ten minutes, all possible air had been expelled from the tube into the bulb. On gently warming the bulb, B, and cooling the tube, A, liquid ether entered, and the absence of air was certain, inasmuch as the ether closed up rapidly and completely, no trace of a bubble being left in the tube. If even a small bubble were left, dissolving in the ether on its way up the sloping tube, the operation was repeated. The silica during this operation usually found its way into the bulb D (fig. 2) at the end of the experimental tube.

The tube was again warmed so as to expel ether. And here arose a difficulty. It was necessary to guess at the quantity of ether which was required. Usually, the experiments were adjusted to suit the particular quantity which accidentally remained. But with a little practice it was found possible to leave in the tube approximately the amount required. The capillary junction, C (fig. 3), between the experimental tube and the bulb was then sealed, leaving a thin tail of glass. The silica was then shaken out of the bulb of the experimental tube (see fig. 1, G, and fig. 2, B) into the tube itself, and distributed along its length as evenly as possible and the experimental tube was then screwed into the pressure apparatus by means of the iron cap for the purpose.

It was found that if mercury entered the space between the rod, D (fig. 2), and the internal wall of the experimental tube, A, it could not be removed by tapping, after the apparatus had been set up; and also that it interfered with the vibrations of the rod. Hence it was necessary to take precautions to prevent mercury entering the tube so far as to touch the end of the rod.

Fig. 2.

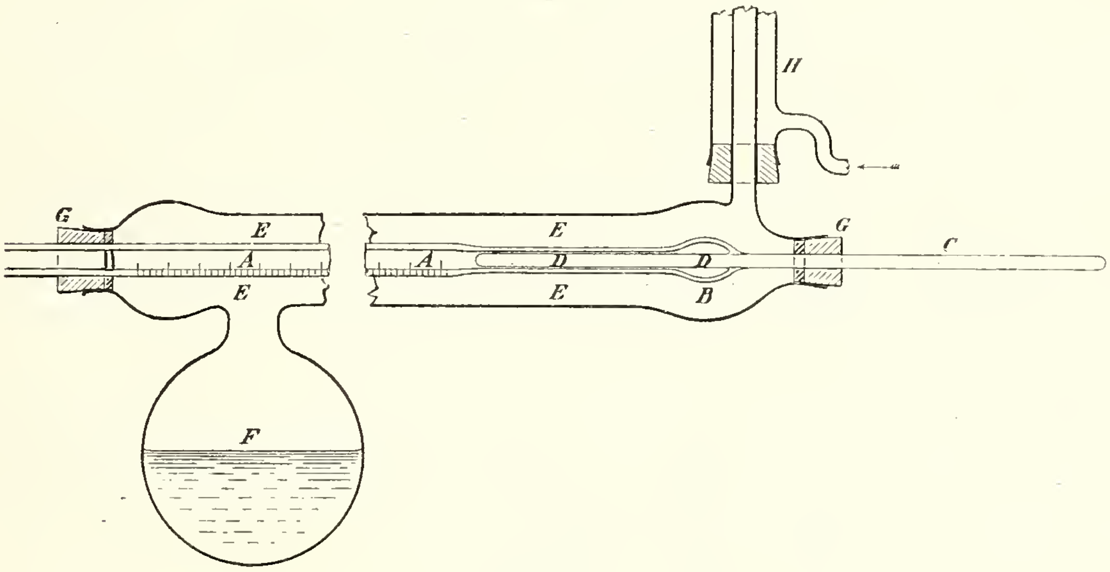
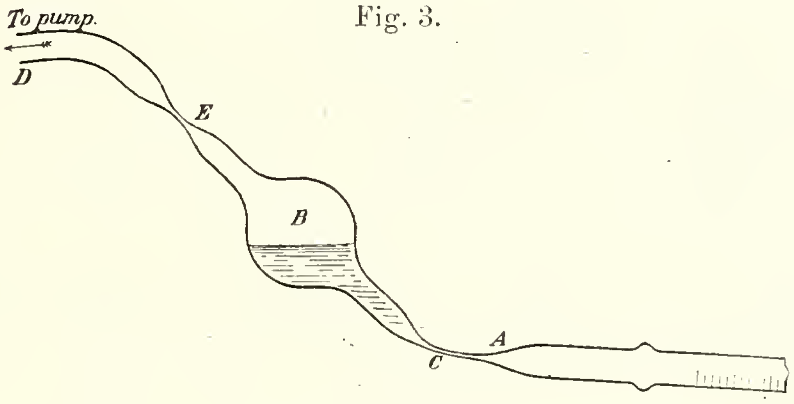


Fig. 3.



The experimental tube having been placed in position in the pressure apparatus, and the cap tightly screwed on, the temperature was raised to a given point, determined by the amount of ether left in the tube; the pressure was then raised by turning the screw of the pressure apparatus A (fig. 1), and when the end of the screw came in contact with the drawn-out capillary end of the experimental tube, C (fig. 3), which is there shown unsealed, it broke it. It was necessary so to regulate the temperature of the ether that only a little escaped when the capillary end was broken. If the pressure in the interior were too great, too much ether escaped; if too small, cold mercury entered, and came in contact with the internal rod. After some practice it was found possible to arrange the apparatus successfully nearly every time. During the breaking of the capillary point, the whole apparatus was tilted, so as to incline the experimental tube. The pressure was then raised so as to cause some mercury to enter the tube, which was then placed in a nearly horizontal position. By tapping, the silica was made to flow down, so as to form an evenly distributed layer in the experimental tube; the temperature was then finally adjusted, and after placing the mercury at a given mark on the tube, experiments were begun. At the temperature chosen the ether was wholly gaseous. On rubbing the projecting rod, the ether gas vibrated, and the silica arranged itself in heaps, which, when the ether gas was at its greatest volume, amounted to over thirty in number. They were, for the most part, regularly distributed. A millimetre scale etched on a slip of mirror, JK (fig. 1), was laid below the experimental tube, and the distance between the heaps was read. But instead of reading the actual position of all the heaps an average was taken in the following manner:—Suppose the total number of heaps to be 30; the 1st and 27th were read; the 2nd and 28th; the 3rd and 29th; and the 4th and 30th; and, dividing by the total number read, four averages were obtained. These usually agreed with each other to within 0·5 per cent.; the mean of all four was taken as the true wave-length.

The middle of each heap of silica was taken as most easily read. The silica could hardly be said to form "heaps"; it distributed itself in streaks of varying length across the tube, each set of streaks forming an oval-shaped patch, of which the middle point could be estimated with fair accuracy.

The volume of the gas was then diminished, and another set of readings taken in a similar manner. The mercury entering the tube covered up a portion of the silica; but on again increasing volume it flowed away, leaving the silica as before. This, of course, made it difficult, if not impossible, to determine accurately the volume occupied by the ether gas; for the volume of the silica was an uncertain quantity. But the whole amount of silica was very small, certainly not amounting in volume to 0·5 per cent. of that of the ether. To compensate for this error, by one in the opposite direction, no correction was made for the increase in volume of the tube on rise of temperature. The error thus introduced is about the same order of magnitude and opposite in sign to that involved by neglecting the volume of the silica, and hence the two errors may be taken as compensating each other to some extent. Moreover, the volume of one gram of ether at definite temperatures and pressures had been determined by Dr. S. YOUNG and one of the authors; and it was necessary to know the actual volume merely for the purpose of deducing the weight.

The volume of the gas was successively decreased, and observations made similar to those described. The temperature having been raised by increasing the pressure on the boiling liquid, a fresh set of observations were made. It was necessary, however, whenever the jacketing vapour was changed, to refill the tube, because the contraction of the ether, owing to its condensation, brought the mercury into contact with the rod, and filled the space between it and the inner wall of the experimental tube. This, of necessity, made the experiments somewhat tedious and difficult; but we venture to think they are as accurate as the method allows.

II. Method of Ascertaining the Weights of Ether Employed.

For each set of experiments with a single jacketing vapour, the tube had to be specially filled with ether. This involved a different weight of ether each time. It was necessary to know the weight, in order to calculate the volume occupied by 1 grm. of the vapour.

To ascertain the weight, the volume at any given pressure and temperature was ascertained from an isothermal diagram showing from previous experiments, by Ramsay and Young, the relations between volume, temperature, and pressure. From this the weight was calculated at each different volume. All the results thus obtained were averaged, and the mean results accepted as the weight.

To take an instance :—At the temperature 140° C., the actual observed volumes and pressure were found as in the first two columns. The volume of 1 grm., corresponding to the pressure in each case, is given in the third column, and is taken from the Memoir referred to; and the weight, calculated from the volume of 1 grm., is to be found in the fourth column. The mean result of all these determinations was taken as the true weight. The volumes of 1 grm. were then calculated by dividing each observed volume by the mean weight. The details of one set of observations are given in the following table :—

Temperature 140° C.				
Pressure.	Actual volume.	Volume of 1 grm. (from diagram).	Weight.	Corrected volumes.
Millims.				
4586	2·279	67·60	·03371	67·29
5070	1·973	60·25	·03275	58·26
5649	1·791	53·00	·03379	52·88
6394	1·552	45·80	·03388	45·82
6798	1·433	42·60	·03364	42·31
7290	1·315	39·00	·03371	38·81
7830	1·197	35·75	·03348	35·34
8725	1·079	31·10	·03470	31·86
9487	0·9615	27·80	·03459	28·39
9912	0·9027	26·20	·03445	26·95

Similar sets of observations at other temperatures with the same ether were taken, and from them the mean weight was ascertained. But it frequently happened that the results at one temperature did not coincide with those at another. It must be remembered that the tube lay horizontally, and that on tilting it, after a set of observations had been made, more ether would escape up the tube. For the hot mercury in passing down gasified ether remaining in that portion of the experimental tube which was inside the pressure apparatus, and the result was that the ether was almost invariably increased somewhat in amount at the higher temperature. Thus, in the above case, calculation of weight at 130° C., 140° C., and 150° C., gave the following numbers as means:—0·03246, 0·03387, 0·03474, the individual results agreeing as closely as those in the preceding table. Each temperature was therefore treated on its merits, and unless no alteration in weight had been proved to occur on changing temperature, the calculations were made on the basis of measurements at different volumes and pressures at the same temperature.

III. Determination of the Frequency of the Vibrating Rod.

Ten sets of experiments were made in order to ascertain accurately the wave-length in air of the note given by the glass rod. The mean result of each is here given; the temperature was 15·5° C.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
19·4	19·5	19·2	19·2	19·3	19·44	19·22	19·71	20·05	19·33

Mean 19·46 millims.

From these results the number of vibrations per second of the rod may be calculated by the formula

$$n = V/\lambda.$$

The velocity of sound in air was taken as 33253 centims. per second at 0° C. ('Encyc. Brit.,' Article *Sound*). The wave-length at 0° is 18·93 millims. Hence $n = 17,566$ per second. The note was a shrill squeak.

The close agreement of the values for the wave-length quoted above seems to show that the accidental sources of error are here only trifling; and they may be considered as practically eliminated from the final mean value. But it is still possible that there may be some constant source of error affecting all the experiments equally; thus it is well known that the wave-length in gases is affected by the diameter of the tube, and this effect may become quite noticeable if the tube is narrow. It is not likely that such an effect really existed in the above experiments, for though the tube was rather narrow, the pitch of the note was exceedingly high. But it was thought as well to make quite certain, and a set of experiments was carried out to test the accuracy of the value of n obtained.

(1.) *Confirmatory Experiments with Hydrogen.*

The velocity of sound in hydrogen has been made the subject of investigation by a large number of experimenters, some of whom used tubes sufficiently wide to obviate all possibility of any marked friction effects occurring. The final result of such experiments is that the velocity of sound in hydrogen is to the velocity in air at the same temperature as the square roots of the specific volumes. Now the mean of nine readings with hydrogen, at 17·5° C., gave 7·36 centims. as the wave-length for the note of the vibrator. Taking the density of air as compared with hydrogen to be 14·47, this gives $n = 17{,}526$ per second as the frequency of the vibrator.

(2.) *Confirmatory Experiments with Argon.*

Experiments were made by one of the authors on the velocity of sound in argon; these experiments were originally undertaken to determine the value of the ratio of the specific heats for argon, but as some observations were carried out with the actual tube described above, they can be used for our present purpose. The following are the measurements observed .—

Mean of 40 readings in original tube with argon at 17·5° C.	1·808 centims.
,, ,, ,, 0°	1·753 ,,
Mean of 6 readings in wider tube with argon at 6·5° C.	3·1 centims.
,, ,, ,, 0°	3·064 ,,
Mean of 5 readings in wider tube with argon at 8·64° C.	3·131 centims.
,, ,, ,, 0°	3·083 ,,
Mean of 11 readings in wider tube with argon at 11·49° C.	3·168 centims.
,, ,, ,, 0°	3·103 ,,
Mean of 5 readings in wider tube with air at 6·7° C.	3·373 centims.
,, ,, ,, 0°	3·332 ,,
Mean of 5 readings in wider tube with air at 7·22° C.	3·41 centims.
,, ,, ,, 0°	3·366 ,,
Mean of 11 readings in wider tube with air at 11·2° C.	3·423 centims.
,, ,, ,, 0°	3·355 ,,

From these numbers we easily find that the mean wave-length at 0° in the wider tube is for argon 3·083 centims., and for air 3·351; this gives us $n = 17{,}452$ in the original tube.

(3.) *Confirmatory Experiments with the Phonograph.*

An attempt was made to discover the number of vibrations emitted per second by the rod with the aid of a phonograph. Such an experiment, if it could have been carried out, would have been extremely valuable as affording a direct determination of the frequency required. Unfortunately, the sound produced by the vibrator was too feeble to make a distinct impression upon the wax cylinder. A long tube of the same kind of glass was, therefore, taken, and this produced a much graver and stronger note, capable of leaving a distinct trace upon the wax; the experiment was also repeated with a shorter tube. The following results were obtained:—

	Length.	No. of points in one revolution.
	millims.	
Tube No. 1 . . .	155·59	766
„ 2 . . .	100·02	1190

A tuning-fork, of frequency 1024, was found to leave 232 impressions in one revolution. This gives as the velocity of sound in this particular kind of glass 263,000 and 262,700 centims. per second for the two tubes respectively.

We may take the mean, 262,850 centims. per second, as the velocity of sound in the glass rod, and this assumption, though we have no guarantee of its exact truth, is unlikely to introduce any serious error. We then find that a rod 28·3 centims. long will emit 18,578 vibrations per second, and this number may be accepted as giving roughly the frequency of the glass rod when performing free vibrations. In the actual apparatus used, the rod was sealed on to a glass tube, near its middle, and this may well have had the effect upon it of a rider on a tuning-fork, and lowered the tone. The test in the present case is, therefore, only a rough one, but it has some value all the same, as it shows that the dust-heaps observed in all these experiments were really due to the vibrations of the fundamental note in air, and not to the higher harmonics in the glass.

It was decided upon the whole to adopt the value of n, derived from the experiments with air, as there is less manipulation required in this case, and, therefore, less liability to experimental error. By comparing the experiments with air, hydrogen, and argon, it will be seen that the value of the frequency is uncertain, to an extent of about $\frac{1}{2}$ per cent.; but it will be shown later on that the particular manner in which this constant enters into the equations renders the uncertainty of far less importance than might at first appear.

IV. Calculations of the Adiabatic Elasticity.

Having ascertained the volume of 1 grm. corresponding to each pressure and temperature observed, and having also found the corresponding mean wave-lengths, the velocity of sound in the ether-gas was calculated by the formula—

$$V = n\lambda,$$

where V is velocity, n the number of vibrations per second, 17,566, and λ the wave-length. The following results were obtained:—

Pressure.	Volume of 1 grm.	Wave-length in millims.	(Velocity in centims. per second)^2.
Temperature 100° C.			
3,932	71·22	11·41	4·0174 × 10^8
4,761	55·97	11·08	3·7884
4,422	61·67	11·00	3·7338
4,843	52·20	10·94	3·6933
4,876	50·35	10·88	3·6528
4,921	Condensed.		
Temperature 110° C.			
4,089	69·49	11·54	4·1190 × 10^8
4,629	60·17	11·41	4·0175
5,016	54·66	11·36	3·9823
5,289	50·93	11·14	3·8296
5,609	47·32	11·04	3·7611
5,905	43·70	11·04	3·7611
6,080	40·08	10·67	3·5131
6,100	Condensed.		
Temperature 120° C.			
4,232	69·50	11·87	4·3478 × 10^8
4,803	60·26	11·65	4·1882
5,218	54·62	11·47	4·0597
5,833	47·32	11·25	3·9054
6,196	43·71	11·37	3·9892
6,623	40·09	10·97	3·7136
7,073	36·50	10·71	3·5396
7,301	34·70	10·60	3·4673
7,452	32·91	10·75	3·5661
7,579	Condensed.		
Temperature 130° C.			
4,378	70·51	12·08	4·5031 × 10^8
4,965	61·06	11·98	4·4288
5,389	55·42	11·49	4·0739
6,073	48·01	11·85	4·3332
6,447	44·34	11·25	3·9054
6,900	40·67	11·25	3·9054
7,424	37·03	11·34	3·9682
8,001	33·39	10·85	3·6327
8,299	31·57	10·44	3·3633
8,683	29·75	10·22	3·2231
9,331	Condensed.		
Second filling. Bromobenzene jacket. Temperature 130° C.			
4,317	70·22	12·06	4·4882 × 10^8
4,940	60·80	11·88	4·3552
5,366	55·26	11·71	4·2314
6,061	47·81	11·43	4·0315
6,432	44·16	11·26	3·9124
6,883	40·50	11·29	3·9332
7,419	36·88	10·86	3·6394
7,971	33·26	10·58	3·4542
9,073	29·62	10·37	3·3184
9,272	27·81	10·30	3·2738
9,445	Condensed.		
Temperature 140° C.			
4,586	67·29	12·28	4·6534 × 10^8
5,070	58·26	12·14	4·5479
5,649	52·88	11·90	4·3699
6,394	45·82	11·73	4·2459
6,798	42·31	11·67	4·2025
7,290	38·81	11·53	4·1023
7,830	35·34	11·48	4·0668
8,725	31·81	11·00	3·7338
9,487	28·39	10·62	3·4883
9,912	26·65	10·56	3·4410
10,373	24·92	10·44	3·3633
Temperature 150° C.			
4,830	65·61	12·37	4·7218 × 10^8
5,451	56·81	12·23	4·6156
5,930	51·56	12·14	4·5479
6,685	44·67	11·94	4·3992
7,147	41·26	11·92	4·3846
7,632	37·84	11·57	4·1308
8,422	34·46	11·44	4·0386
9,281	31·07	11·21	3·8778
10,098	27·68	10·83	3·6193
11,074	24·29	10·75	3·5661
Third filling. Bromobenzene jacket. Temperature 140° C.			
10,898	23·00	10·06	3·1230 × 10^8
11,550	21·20	9·87	3·0061
11,618	20·90	9·59	2·8439
11,675	20·75	9·70	2·9034
Temperature 150° C.			
11,401	22·80	10·55	3·4346 × 10^8
12,469	19·80	10·14	3·1729
Fourth filling. Fresh ether. Aniline jacket. Temperature 150° C.			
5,483	57·10	12·28	4·6534 × 10^8
6,733	44·88	12·00	4·4436
7,627	38·88	11·67	4·2025
8,657	32·94	11·43	4·0315
10,081	27·04	11·06	3·7746
Temperature 160° C.			
5,719	56·39	12·43	4·7677 × 10^8
7,051	44·32	12·03	4·4659
7,973	38·40	11·89	4·3624
9,048	32·53	11·78	4·2822
9,413	26·70	11·33	3·9612

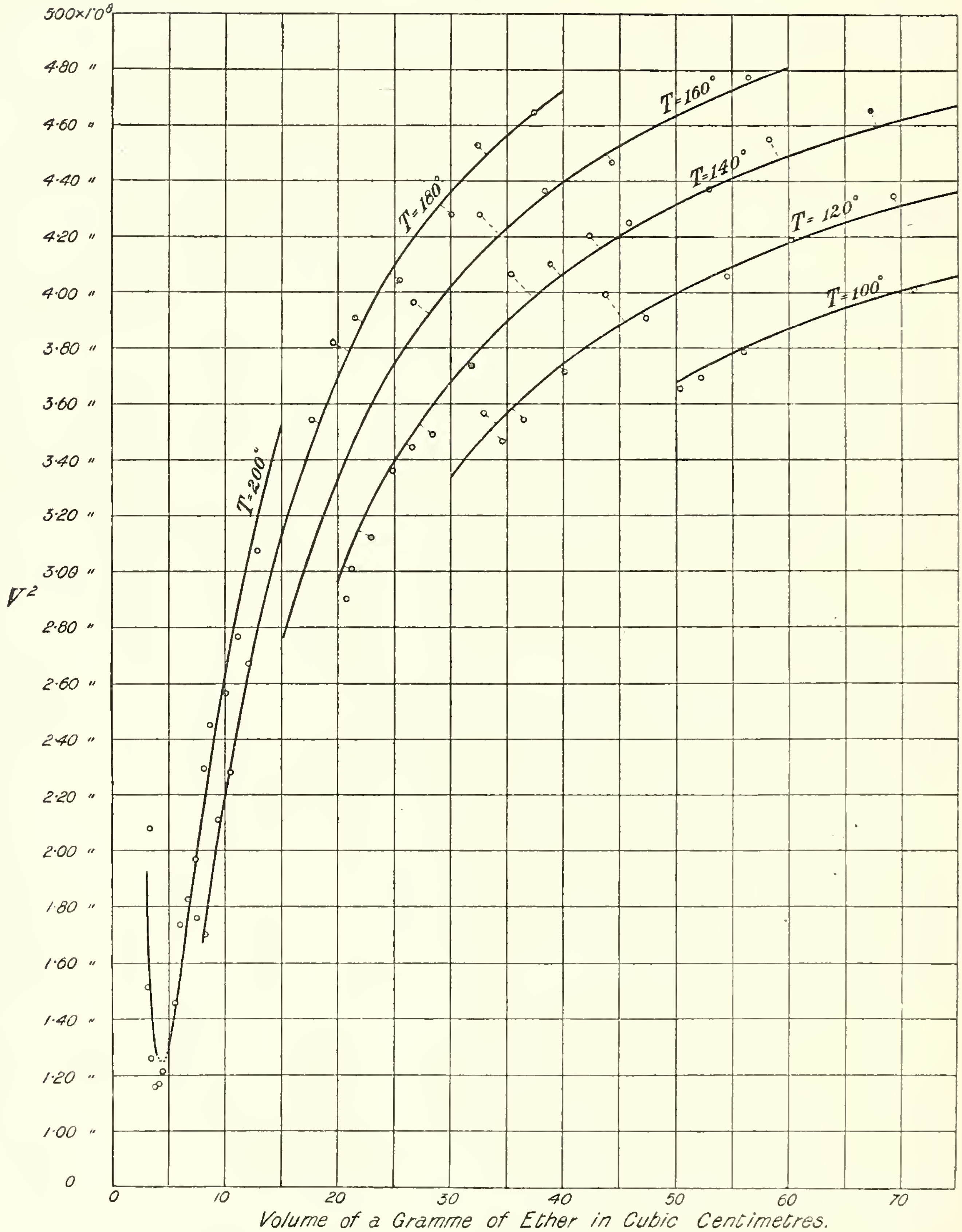
Pressure.	Volume of 1 grm.	Wave-length in millims.	(Velocity in centims. per second)^2.
Fifth filling. Aniline jacket. Temperature 170° C.			
18,195	12·13	9·14	$2·5779 \times 10^8$
18,649	11·48	8·56	2·2611
19,112	10·83	8·08	2·3249
19,191	10·05	7·97	1·9602
Temperature 180° C.			
19,339	12·04	9·30	$2·6689 \times 10^8$
20.596	10·42	8·59	2·2769
21,471	9·46	8·26	2·1054
22,481	8·20	7·42	1·6990
22,533	7·57	7·55	1·7590
Temperature 185° C.			
19,756	12·06	9·52	$2·7903 \times 10^8$
21,177	10·44	8·80	2·3896
22.135	9·48	8·30	2·1258
23,267	8·21	7·74	1·8486
23,847	7·58	7·37	1·6380
24,305	6 96	6·90	1·4692
24,368	6·33	6·65	1·3646
Sixth filling. Aniline jacket. Temperature 150° C.			
7,845	37 07	12·23	$4·6156 \times 10^8$
8,893	32·10	11·27	3·9193
9,578	29·13	11·00	3·7338
10,626	25·24	10·64	3·4934
11,232	23·31	10·37	3·3184
11,884	21·38	10·28	3·2610
12,025	19·47	10·25	3·2420
13,371	17·55	9·67	2·8856
13,687	16·60	9·58	2·8321
Temperature 170° C.			
8,509	36·95	11·94	$4·3992 \times 10^8$
9,526	31·99	11·83	4·3185
10,276	29·04	11·55	4·1165
11,477	25·16	11·15	3·8363
12,890	21·31	10·90	3·6663
14,656	17·50	10·39	3·3313
19,246	Condensed.		
Temperature 180° C.			
8,755	37·35	12·27	$4·6467 \times 10^8$
9,854	32·35	12·12	4·5328
10,644	30·04	11·78	4·2822
11.893	25·44	11·44	4·0386
13,398	21·55	11·25	3·9054
14,268	19·62	11·12	3 8157
15,294	17·69	10·71	3·5396

Pressure.	Volume of 1 grm.	Wave-length in millims.	(Velocity in centims. per second)^2.
Seventh filling. Quinoline jacket. Temperature 185° C.			
19,650	12·27	9·26	$2·6460 \times 10^8$
21,056	10·63	8·75	2·3626
21,914	9·65	8·32	2·1360
22,488	9·00	7·91	1·9308
22,671	8·36	8·92	1·9848
23,281	7·72	7·63	1·7964
Temperature 190° C.			
20,119	12·44	9·51	$2·7908 \times 10^8$
21,583	10·77	9·06	2·5330
22,613	9·77	8·52	2·2400
23,904	8·47	7·96	1·9552
24,530	7·82	7·64	1·8012
25,028	7·17	7·35	1·6671
25,478	6·53	7·00	1·5121
26,372	5·89	6·76	1·4102
Temperature 193·8° C.			
20,495	12·42	9·65	$2·8736 \times 10^8$
22,085	10·75	9·17	2·5948
23,107	9·76	8·90	2·4443
24,466	8·45	8·21	2·0799
25,205	7·81	7·86	1·9064
25,904	7·16	7·50	1·7358
26,235	6·52	7·17	1·5864
26,860	5·88	6·92	1·4777
27,302	4·92	6·14	1·1633
27,357	4·60	6·31	1·2286
Temperature 195° C.			
20,613	12·42	9·75	$2·9334 \times 10^8$
22,188	10·88	9·24	2·6346
23,260	9·76	8·90	2·4443
24,679	8·45	8·83	2·0952
25,315	7·81	7·91	1·9308
26,583	6·52	7·22	1·6086
27,144	5·88	7·04	1·5294
27,518	5·24	6·74	1 4018
Temperature 200° C.			
21,056	12·81	9·98	$3·0735 \times 10^8$
22,739	11·09	9·47	2·7674
23,806	10·06	9·12	2·5666
25,252	8·72	8·39	2·4498
26,024	8·05	8·62	2·2929
26,707	7·39	7·99	1·9700
27,438	6·73	7·69	1·8249
28,082	6·06	7·50	1·7358

Pressure.	Volume of 1 grm.	Wave-length in millims.	(Velocity in centims. per second)^2.
Eighth filling. Saturated vapour. Temperature 190° C.			
26,030	5·577	6·79	1·4227 $\times 10^8$
26,026	4·830	6·75	1·4060
Temperature 193·8° C.			
27,538	5·577	6·35	1·2433 $\times 10^8$
27,595	4·830	6·26	1·2092
27,595	4·383	6·09	1·1445
27,595	4·088	6·23	1·1977
27,646	3·798	6·22	1·1938
27,584	3·508	6·36	1·2482
27,584	3·217	6·55	1·2938
27,674	2·929	6·63	1·3564
27,758	2·929	7·07	1·5424
28,291	2·785	8·50	2·2295
29,722	2·641	10·45	3·3699
Temperature 195·15° C.			
27,949	5·577	6·48	1·2957 $\times 10^8$
28,147	4·830	6·13	1·1452
28,233	4·383	5·95	1·0925
28,258	4·088	5·85	1·0561
28,288	3·798	5·60	0·9677
28,389	3·508	5·47	0·9233
Temperature 193·8° C.			
27,441	5·577	6·35	1·2443 $\times 10^8$
27,605	4·830	6·37	1·2521
27,553	4·383	6·27	1·2131
27,553	4·088	6·21	1·1900
27,553	3·798	6·41	1·2679
Liquid.			
27,553	3·798	6·08	1·1407 $\times 10^8$
27,553	3·508	6·25	1·2054
27,553	3·217	6·31	1·2287
27,580	2·929	6·65	1·3646
27,627	2·856	6·75	1·4060
27,958	2·785	7·93	1·9405
28,415	2·713	8·22	2·0850
28,817	2·641	9·15	2·5835
29,702	2·584	10·06	3·1230
Temperature 195·15° C.			
27,888	5·577	6·49	1 2997 $\times 10^8$
28,140	4·830	6·28	1·2561
28,166	4·383	6·19	1·1824
28,195	4·088	6·02	1·1183
28,206	3·798	5·44	0·9132
28,222	3·508	5·26	0·8538
28,275	3·362		
28,337	3·217		
28,598	3·073		
28,857	2·929		
29,253	2·856		
29,679	2·785		
30,358	2·713		
Temperature 195·15° C.			
28,235	3·362	5·24	0·8473 $\times 10^8$
28,278	3·217	5·57	0 9574
28,337	3·073	5·80	1·0381
28,598	2·929	6·99	1·5078
28,857	2·856	7·62	1·7918
29,253	2·785	8·54	2·2506
29,679	2·713	8·70	2·3357
30,358	2·641	9·72	2·9155
Temperature 195·15° C.			
27,968	5·577	6·45	1·2838 $\times 10^8$
28,137	4·830	6·07	1·1370
28,165	4·383	5·92	1·0815
28,207	4·088	5·72	1 0096
28,223	3·798	5·49	0·9301
28,223	3·508	5·18	0·8280
28,311	3·217	5·42	0·9065
28,625	2·929	7·06	1·5380
28,892	2·856	7·51	1·7404
29,158	2·785	8·50	2·2295
29,649	2·713	8·97	2·4829
30,225	2,641	9·91	3·0305
Temperature 200° C.			
29,432	5·577	6·82	1·4353 $\times 10^8$
29,870	4·830	6·39	1·2600
29,964	4·383	6·26	1·2092
30,258	4·088	6·16	1·1709
30,355	3·798	6·13	1·1596
30,457	3·508	6·39	1·2600
30,823	3·217	7·00	1·5121

From these observations a set of isothermal curves was constructed, where V^2 was plotted against volume (see fig. 4). The results are not very concordant; some

Fig. 4.



are altogether erratic, and this is to be expected, for it was not always possible so to rub the rod as to produce the required tone. A rod so placed is capable of many kinds of vibrations, and the particular rate of vibration, though the one most usually produced, may, by some difference in the method of rubbing, be replaced by another.

But, on the whole, the resulting curves show good concordance. Where a number of curves such as these, differing from each other by regular intervals, is drawn, the position of each of them lends control to that of its neighbour, and a close approximation to accuracy may be deduced from very unpromising material.*

These curves were then further utilized by reading off the values of V^2 for equal volumes, 70, 65, 60, and so on, at intervals of 5 down to volume 20 cub. centims. per grm., and at smaller intervals, viz., 17·5, 15, 14, 13 cub. centims. per grm., and so on, down to 4 cub. centims. per grm. at smaller volumes.

From these numbers a second diagram was constructed, representing the values of V^2/v plotted against temperature, the lines being isochoric. These curves were observed not greatly to deviate from straight lines—they intersected at small volumes. They would probably also intersect at larger volumes if produced. It has not been thought necessary to reproduce this figure as it is virtually contained in fig. 4.

The value of V^2/v is, of course, the same as the adiabatic elasticity, and, like the isothermal elasticity, it has the dimensions of a pressure. It will be remembered that V was measured in centimetres per second, and v in cub. centims. per grm. Consequently, the elasticity, as calculated above, must be given in absolute units, or dynes per sq. centim. It was found more convenient to change to pressures measured in millimetres of mercury, and this can be readily done by dividing all the former numbers by 1334·2.

V. MATHEMATICAL DISCUSSION OF PRECEDING RESULTS.

We noticed above that for equal volumes the adiabatic elasticity is roughly a linear function of the temperature, and this fact seems to hold out some hope of bringing all the experimental results obtained under the power of analysis. An inspection of the diagram shows that the difference between the isochorals actually drawn and straight lines is no greater than the uncertainty due to experimental errors, so that as far as the direct evidence goes it is possible that the isochorals are really straight. Even if it should turn out on subsequent investigation that the isochorals are slightly curved, the treating them as straight lines may be considered as a first approximation to the truth, and as a justifiable simplification of a very complex problem.

Let us call the adiabatic elasticity measured in millimetres of mercury E, then we may put

$$E = gT - h,$$

where g and h are functions of the volume only. Now, it was shown by one of the authors, in conjunction with Dr. SYDNEY YOUNG, that for constant volumes there is a linear relation between the temperature and pressure, so that we may put

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* The curves actually given in fig. 4 have been calculated by means of the formula on p. 183; they are the smoothed version of a set of similar curves drawn to represent the actual observations. They agree with the observations better than the original free-hand curves.

$$p = b\mathrm{T} - a,$$

where b and a are functions of the volume only ('Phil. Mag.,' vol. 23, p. 436). From these two equations it is possible to eliminate the temperature, and we obtain

$$\mathrm{E} = \frac{g(p+a)}{b} - h,$$

$$= \frac{g}{b}p - h + \frac{ga}{b}.$$

Thus we see that for constant volumes E may be expressed as a linear function of p; the next step is evidently to find the value of g/b. For this purpose the isochoral diagram was employed; a straight edge was laid so as to pass as near as might be to the drawn points, and the slope of this edge was then determined; this slope gave the value of g. To obtain b nothing more was needed than to use the values given in RAMSAY and YOUNG's paper (*loc. cit.*, p. 441). On calculating the value of g/b for various volumes, it was found to be nearly constant; such deviations as existed were not arranged in any orderly manner, but occurred sometimes to one side and sometimes to another, as if fluctuating about a mean value. It appeared as if $g/b = 11/9$ might be taken as a fair mean between all the values obtained. We may therefore put

$$\mathrm{E} = \frac{11}{9}p - h + \frac{11}{9}a,$$

and this leads to the equation

$$\mathrm{V}^2 = 1631\,pv - f(v),$$

where $f(v)$ is a function of v only. In order to determine the value of $f(v)$, the above was written

$$f(v) = 1631\,pv - \mathrm{V}^2.$$

Keeping the volume constant, and changing the temperature, this equation gives values of $f(v)$ differing slightly from one another; the arithmetical mean was chosen as giving the value of $f(v)$ for that particular volume. In this way $f(v)$ was determined for a large number of volumes, and it was found that its values could be approximately represented by means of the empirical formula

$$f(v) = \frac{785{,}300{,}000}{v^{2/3}} - \frac{317{,}700{,}000}{v^{4/3}} - \frac{3{,}114{,}000{,}000}{v^2}.$$

The above formula was selected from a large number that were tried, and it reproduced the found values of $f(v)$ fairly well, but it is not suggested as being anything more than an empirical formula. Unfortunately the Kinetic Theory of Gases is not sufficiently advanced to enable us to form any *à priori* notion as to what form the function $f(v)$ might be expected to have, so that we are perforce driven to employ an empirical formula. With a large amount of time and labour it might be possible to find a formula for $f(v)$ simpler in character, and more exact in its results, but it did not seem worth while to undertake the amount of trouble involved in such a search. The formula can be successfully used for the purposes of interpolation within the field of observation, but any use of it for extrapolation would be hazardous.

We may now write the equation for V^2 as

$$V^2 = 1631\,pv - \frac{785{,}300{,}000}{v^{2/3}} + \frac{317{,}700{,}000}{v^{4/3}} + \frac{3{,}114{,}000{,}000}{v^2}.$$

This formula has been obtained as the result of four consecutive approximations, and it is possible that each succeeding approximation has led us further from the facts. On the other hand, it is conceivable that the errors of the various approximations have to a large extent neutralised one another. It was thought advisable therefore to test the above formula by calculating out the isothermals, and comparing them with the observed measurements. The result is shown in fig. 4; and it is easily seen that the calculated isothermals may be fairly taken as a system of smooth lines passing through the observed points.

From the equation to V^2 we obtain

$$E = \frac{11}{9}p - \frac{785{,}300{,}000}{1334{\cdot}2}\,v^{-5/3} + \frac{317{,}700{,}000}{1334{\cdot}2}\,v^{-7/3} + \frac{3{,}114{,}000{,}000}{1334{\cdot}2}\,v^{-3},$$

or,

$$-v\frac{dp}{dv} = \frac{11}{9}p - \frac{588{,}600}{v^{5/3}} + \frac{238{,}100}{v^{7/3}} + \frac{2{,}334{,}000}{v^3}.$$

Multiply by $-v^{2/9}$ and we get

$$v^{11/9}\frac{dp}{dv} + \frac{11}{9}pv^{2/9} = \frac{588{,}600}{v^{13/9}} - \frac{238{,}100}{v^{19/9}} - \frac{2{,}334{,}000}{v^{25/9}}$$

Integrating

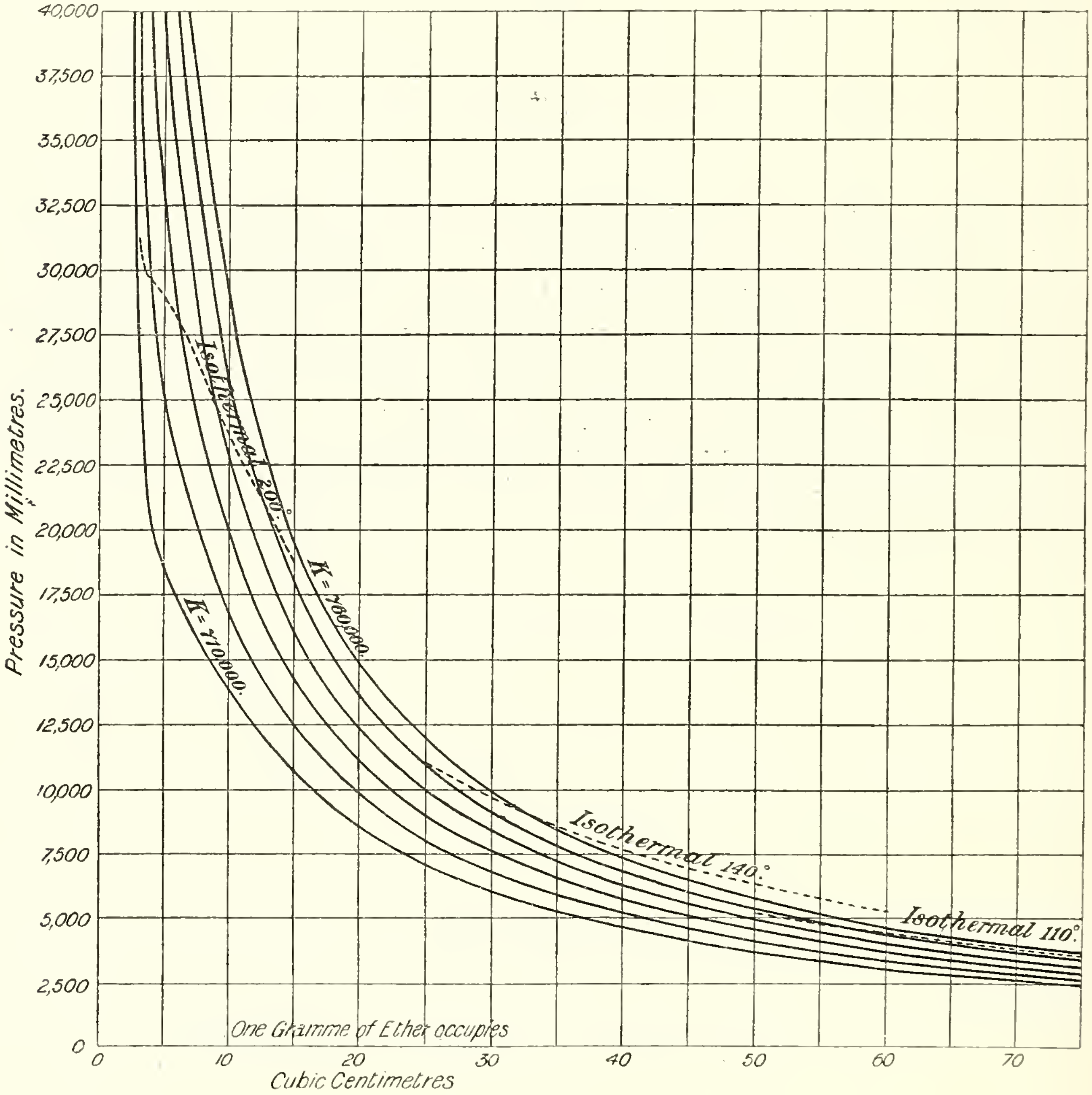
$$pv^{11/9} = k - \frac{9}{4} \times \frac{588{,}600}{v^{4/9}} + \frac{9}{10} \times \frac{238{,}100}{v^{10/9}} + \frac{9}{16} \times \frac{2{,}334{,}000}{v^{16/9}}.$$

Hence,

$$p = \frac{k}{v^{11/9}} - \frac{1{,}324{,}000}{v^{5/3}} + \frac{214{,}300}{v^{7/3}} + \frac{1{,}313{,}000}{v^3}.$$

The constant k is at our disposal, and we may choose it so that the adiabatic shall pass through any assigned point. By giving a series of different values to k we obtain a system of adiabatic lines. We may get a convenient system by giving to k successively the values 710,000, 720,000, 730,000, 740,000, 750,000, 760,000 ; such a system is shown in fig. 5 ; the curves have been drawn for a great part of their length so as to exhibit to the eye their general shape, but only that portion of the system which is intersected by the drawn isothermals has been really investigated experimentally, and can, therefore, be safely trusted. The adiabatic for $k = 720{,}000$ passes close to the critical point.

Fig. 5.



The system of isothermals and adiabatics intersecting one another divides the plane of pv into a set of curvilinear parallelograms, such as that suggested in MAXWELL's 'Theory of Heat' (p. 156); and, if our interpretation of the experimental results is correct, it ought to be possible so to select the system of adiabatics that the areas of all the parallelograms are equal. The following thermo-dynamic investigation will show to what extent this can be done.

Let us assume that the equation to the isothermals of a gas can be written in the form

$$p = b\mathrm{T} - a,$$

where b and a are functions of the volume only. Let us also assume that the equation for the adiabatic elasticity E can be put in the form

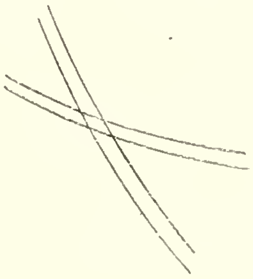
$$\mathrm{E} = g\mathrm{T} - h,$$

where g and h are functions of the volume only. Then, by eliminating T, and putting for E its value $- v \dfrac{dp}{dv}$, we see that we have a linear differential equation for p of the first order, the independent variable being v. The integral of such an equation must be of the form

$$p = k\psi + \chi,$$

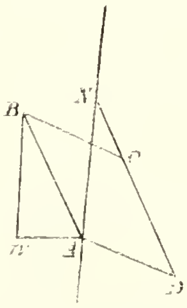
where k is the constant of integration, while ψ and χ are functions of v only; we see also that we must have $\psi'/\psi = - g/bv$. This equation determines a system of adiabatics by giving successively different values to k, and by taking two neighbouring values, say k and $k + dk$, we obtain two adiabatics as near together as we please. Let now the pair of adiabatics be crossed by two isothermals at temperatures T and T + dT, then the area of the infinitely small parallelogram formed must be independent of T by the Second Law of Thermo-dynamics.

Fig. 6.



Let ABCD in fig. 7 denote a magnified picture of this small parallelogram; then, by shearing the figure after the manner of Maxwell in obtaining his fourth thermodynamical relation (*loc. cit.*, p. 166), we obtain

Fig. 7.



area ABCD = increase of pressure when we pass from lower to higher adiabatic at constant volume.

× increase of volume when we pass from higher to lower isothermal along adiabatic.

$$= -\psi\, dk \times \left(\frac{dv}{d\mathrm{T}}\right)_k d\mathrm{T}.$$

Now, whatever the variations of pressure volume and temperature, they are subject, if small, to the relation

$$dp = b\, d\mathrm{T} + \left(\mathrm{T}\frac{db}{dv} - \frac{da}{dv}\right) dv.$$

Let us denote differentiation with regard to v by accents, then we may put this

$$dp = b\, d\mathrm{T} + (b'\mathrm{T} - a')\, dv.$$

Also any adiabatic alteration will be subject to the relation

$$dp = (k\psi' + \chi')\, dv.$$

Hence,

$$b\, d\mathrm{T} + (b'\mathrm{T} - a')\, dv = (k\psi' + \chi')\, dv$$

$$\left(\frac{dv}{d\mathrm{T}}\right)_k = \frac{b}{k\psi' + \chi' + a' - b'\mathrm{T}} = \frac{b}{k\psi' + \chi' + a' - b'\dfrac{p + a}{b}}$$

$$= \frac{b}{k\psi' + \chi' + a' - \dfrac{b'a}{b} - \dfrac{b'}{b}(k\psi + \chi)} = \frac{b}{k\left(\psi' - \dfrac{b'}{b}\psi\right) + \chi' + a' - \dfrac{b'}{b}(\chi + a)}.$$

Therefore

$$-\psi(v)\left(\frac{dv}{d\mathrm{T}}\right)_k = \frac{b\psi}{k\left(\psi\dfrac{b'}{b} - \psi'\right) + \dfrac{b'}{b}(\chi + a) - \chi' - a'}.$$

Now this quantity is to be independent of T so long as we keep k unaltered, hence we have

$$k\left(\frac{b'}{b^2} - \frac{\psi'}{b\psi}\right) + \frac{b'}{b^2\psi}(\chi + a) - \frac{\chi' + a'}{b\psi} = \text{function of } k \text{ only}.$$

This can only be the case if the expressions $\dfrac{b'}{b^2} - \dfrac{\psi'}{b\psi}$, $\dfrac{b'}{b^2\psi}(\chi + a) - \dfrac{\chi' + a'}{b\psi}$ are functions of k only. But both these expressions, from their form, can be seen to be functions of v only; hence they must be numerical constants. Let

$$b'/b^2 - \psi'/b\psi = \mathrm{C}, \text{ say},$$

then

$$b'/b - Cb = \psi'/\psi.$$

Substituting for ψ'/ψ, we may write this

$$b'/b - Cb = -g/bv,$$

so that

$$g = Cb^2v - b'v.$$

As long as there is no assumption made about the connection between g and b, this equation simply gives g in terms of b. The adiabatics we have drawn, however, were the result of further assuming that g/b is equal to a constant; and if this condition is introduced, we find that the form of b is restricted. Let us denote by γ, the constant value of g/b, then

$$b'/b^2 + g/b^2v = C, \quad \text{or} \quad b'/b^2 + \gamma/bv = C.$$

Put $1/b = u$, and we have

$$du/dv - \gamma u/v = -C.$$

This equation is easily integrated, and we obtain

$$u = \frac{1}{R}(v + ev^\gamma),$$

so that

$$b = \frac{R}{v + ev^\gamma},$$

where R and e are constants at our disposal.

If we confine ourselves to volumes which lie between 70 and 4, the values of b may be roughly reproduced by means of the above formula, taking care to give suitable values to R and e. But if, in such a formula, we were to attempt to extrapolate to large volumes, the result would be that we should obtain values of b totally at variance with experiment. This shows us once more the need of restricting our formulæ entirely to those portions of the field that have been experimentally investigated.

APPENDIX.

Experiments with Liquid Ether.

In experimenting with liquid ether, the apparatus and method of working were similar in every respect to what has already been described.

The volume of 1 grm. of the ether was, as before, not directly determined, but was inferred from a knowledge of temperature and pressure. It was more easy to obtain well-defined heaps of silica in the liquid than in the gas.

The following results were obtained :—

Pressure.	Volume of 1 grm.	Wave-length in millims.	(Velocity in centims. per second)^2.
	Temperature 100° C.		
4,859	1·638	37·67	43·786 $\times 10^8$
15,834	1·6225	38·20	45·026
28,665	1·610	40·43	50·436
	Temperature 120° C.		
7,496	1·735	32·42	32·431 $\times 10^8$
15,823	No data	33·50	34·707
28,644	,,	35·25	38·341
	Temperature 150° C.		
13,281	1·931	23·33	16·794 $\times 10^8$
15,861	1·913	24·53	18·567
18,550	1·903	25·00	19·285
21,595	1·894	25·47	20·017
28,712	1·870	27·34	23·064
	Temperature 175° C.		
19,998	2·218	15·27	7·195 $\times 10^8$
21,625	2·208	15·61	7·519
23,565	2·176	16·64	8·544
28,753	2·110	18·54	10·606
	Temperature 185° C.		
23,356	2·490	10·93	3·686 $\times 10^8$
24,677	2·424	12·52	4·859
25,898	2·376	13·23	5·401
27,250	2·330	14·42	6·416
28,753	2·299	15·19	7·120
30,431	2·262	15·97	7·869
32,313	2·229	16·84	8·750
	Temperature 190° C.		
25,074	2·730	8·35	2·151 $\times 10^8$
25,867	2·668	9·81	2·969
27,250	2·546	11·61	4·159
28,753	2·463	12·81	5·063
30,431	2·398	14·04	6·082
32,313	2·342	15·18	7·110
36,681	2·256	17·12	9·044
	Temperature 195° C.		
25,898	*	7·14	1·573 $\times 10^8$
27,250	3·285	7·22	1·608
28,753	2·779	9·58	2·832
30,431	2·601	11·28	3·926
32,313	2·501	12·79	5·047
34,441	2·426	14·07	6·108
36,681	2·366	15·31	7·233
39,700	2·307	16·50	8·400
	Temperature 200° C.		
30,431	3·282	8·20	2·075 $\times 10^8$
32,313	2·803	10·28	3·261
34,441	2·632	11·90	4·370
36,681	2·520	13·46	5·590
39,700	2·415	15·00	6·943
	Temperature 205° C.		
30,398	*	6·67	1·373 $\times 10^8$
33,282	3·314	7·62	1·792
34,409	2·931	9·84	2·988
36,681	2·721	11·62	4·166
39,658	2·565	13·13	5·319
	Temperature 210° C.		
32,282	*	7·10	1·555 $\times 10^8$
34,409	3·535	7·88	1·916
36,681	3·122	9·83	2·981
39,658	2·788	11·57	4·131

Treating these data as before, the isochoric lines for V^2/v are found to be straight. The investigation was not pushed further, however, as the formulæ involved appeared to be even more complicated than in the case of the larger volumes; but the above experimental data have been given for the sake of anyone who feels interested in the subject.

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* Volume not read; curve nearly horizontal.

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VIII. *On the Relation between Magnetic Stress and Magnetic Deformation in Nickel.*

By E. TAYLOR JONES, *D.Sc.*

Communicated by Professor ANDREW GRAY, *F.R.S.*

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THE object of the experiments described below was to determine how much of the contraction, which occurs in a nickel wire when magnetised, is due to stresses brought into play by magnetisation. This has been attempted by several experimenters, but it has been assumed by some that the magnetic stress concerned is a contracting stress of magnitude $B^2/8\pi$, an assumption which has only recently been shown to be unjustifiable.[*]

That the system of stresses in a magnetic field, described by MAXWELL ("Electricity and Magnetism," Art. 642) as explaining the observed forces between magnetic bodies, is not sufficient to account for the observed deformation of bodies in the field, is clear from the fact that these stresses increase continually with the magnetisation and field-strength, while the deformation in iron and cobalt becomes reversed when the field reaches a certain value. It can also be shown that MAXWELL's stresses would produce no change in the dimensions of a ring magnetised by a uniform circumferential field, whereas BIDWELL[†] has found considerable change both in the diameter and the volume of rings of iron.

The theory of magnetic stress has, however, been extended, chiefly by v. HELMHOLTZ,[‡] KIRCHHOFF,[§] Professor J. J. THOMSON,[||] and HERTZ,[¶] who have shown that, in addition to MAXWELL's distribution of stress, there are other stresses in a magnetised body due to the fact that the magnetisation depends upon the strain in the body.

Hitherto no direct experiments have been made with the object of ascertaining whether these stresses, in addition to those of MAXWELL, are sufficient to account for the observed deformation of bodies placed in a magnetic field. The facts that "Villari reversals" of opposite kinds exist in iron and cobalt, and also opposite reversals of magnetic deformation, and that in nickel (at any rate at moderate field-strengths) there is neither Villari reversal nor reversal of deformation, suggest that there is a close connexion between the two phenomena, and this general similarity between the effects of stress on magnetisation, on the one hand, and magnetic deformation on the other, has led some experimenters to assume that magnetic deformation is completely accounted for by the above stresses, and to calculate from the observed deformation the general effect of stress on magnetisation.*

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[*] C. CHREE, 'Nature,' January 23, 1896; H. NAGAOKA and E. T. JONES, 'Phil. Mag.,' May, 1896.

[†] S. BIDWELL, 'Proc. Roy. Soc.,' vol. 55, p. 228; vol. 56, p. 94.

[‡] 'Wied. Ann.,' vol. 13, p. 400, 1881.

[§] 'Wied. Ann.,' vol. 24, p. 52, 1885.

[||] 'Applications of Dynamics to Physics and Chemistry,' p. 48, 1888.

[¶] 'Ausbreitung der Elektrischen Kraft,' p. 275, 1892.

Before this assumption can be legitimately made, however, it is necessary to make direct experiments to test its truth, and it was with this object that the following experiments were instituted.

The experiments were made in the Physical Laboratory of the University College of North Wales, and, before proceeding to describe them, I wish here to express my great indebtedness to Professor A. GRAY for kindly placing at my disposal all the necessary apparatus, and for many valuable suggestions.

Theory.

One method of experimenting, suggested by Mr. NAGAOKA and the present writer,† would be to measure both the effect of hydrostatic pressure on magnetisation and the magnetic deformation of a ring of soft magnetic material. From these measurements a direct comparison could be made of the observed deformation and the value calculated from the theory of KIRCHHOFF.

There is however another method which, though theoretically not so simple, is probably easier to carry out experimentally. It has been shown by CANTONE‡ that the elongation δl of an ellipsoid of revolution of great eccentricity and soft magnetic material, when placed in a uniform longitudinal field H is, on KIRCHHOFF's theory, given by

$$\frac{\delta l}{l} = \frac{4\pi \mathrm{I}^2}{3\mathrm{E}}\left(\frac{1+\theta}{1+2\theta}\right) + \frac{\mathrm{IH}}{2\mathrm{E}(1+2\theta)} - \frac{\kappa' \mathrm{H}^2}{2\mathrm{E}(1+2\theta)} - \frac{\kappa'' \mathrm{H}^2}{2\mathrm{E}} \quad . \quad . \quad . \quad (1),$$

where

l = length of ellipsoid,

I = magnetisation,

κ', κ'' are the coefficients of change of magnetic susceptibility with change of density and of elongation§ respectively,

E = YOUNG's Modulus for the material, and θ is defined by

$$\frac{\mathrm{E}}{2}\,\frac{1+2\theta}{1+3\theta} = \text{rigidity} = n.$$

---

* CANTONE, 'Mem. R. Acc. Linc.,' ser. 4, vol. 6, 1890; WINKELMANN, 'Handbuch der Physik,' Bd. 3, Part II., p. 250, 1895.

† *Loc. cit.*, p. 461.

‡ *Loc. cit.*

§ The fundamental equation defining κ' and κ'' is $\mathrm{I} = \{\kappa - \kappa'(e+f+g) - \kappa'' e\}\,\mathrm{H}$, where e, f, g are the dilatations parallel to the direction of magnetisation, and to two axes at right angles to it.

It can also be shown that if a tension δP per unit area be applied to a long uniform wire of the material and produce a small increase δI in the magnetisation, then

$$\frac{E}{H}\frac{\delta I}{\delta P} = -\frac{\kappa'}{1+2\theta} - \kappa'' \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2).$$

Between (1) and (2) the quantity $\left(\frac{\kappa'}{1+2\theta} + \kappa''\right)$ can be eliminated, and the resulting equation is

$$\frac{\delta l}{l} = \frac{4\pi I^2}{3E}\cdot\frac{1+\theta}{1+2\theta} + \frac{IH}{2E(1+2\theta)} + \tfrac{1}{2} H \frac{\delta I}{\delta P} \quad . \; . \; . \; . \; . \; . \quad (3).$$

In order to compare this result with experiment a long cylindrical specimen should first be used to determine I and $\delta I/\delta P$ for several constant field-strengths. Then the specimen should be turned down to the form of an ellipsoid of revolution and the magnetic elongation α[*] measured with the specimen in the same magnetic state as that in which I and $\delta I/\delta P$ were determined.

At first it was intended to do this, but afterwards it was thought sufficient to use a wire of the material (of length very great in comparison with its thickness) in both parts of the experiment, thus assuming that the elongation of a long thin wire is the same as that of an ellipsoid of revolution having the same dimensional ratio.[†] The general agreement between the results of different experimenters, who in measuring magnetic elongation have used wires, strips and ellipsoids of various shapes and degrees of purity, shows that this is at least approximately the case.

It can also be proved independently that in a uniformly magnetised wire the term $\frac{1}{2}H\frac{\delta I}{\delta P}$, which is generally by far the greatest on the right-hand side of (3), represents the elongation due to those stresses which arise in consequence of the fact that magnetisation depends upon strain. For the potential energy, which unit volume has in consequence of the magnetisation, is $-\frac{1}{2}HI$.[‡] Hence, if the body has dilatations e, f, g, parallel to the axes of x, y, z, respectively, the part of the Lagrangian Function depending on magnetisation and strain coordinates is (supposing the quantities to vary infinitely slowly)

$$L = \tfrac{1}{2}HI - \tfrac{1}{2}m(e+f+g)^2 - \tfrac{1}{2}n(e^2+f^2+g^2-2ef-2fg-2ge).\text{§}$$

---

[*] The symbol α is here used for the observed elongation of the specimen, *i.e.* the ratio of the observed increase of length to the whole length.

[†] A change in the state of the surface of the specimen would be caused by the turning down, which would make that process inadvisable.

[‡] MAXWELL, "Electricity and Magnetism," vol. 2, § 632.

[§] J. J. THOMSON, *loc. cit.*

Professor J. J. THOMSON has shown that the strains due to the dependence of magnetisation upon strain are given by the equations

$$\partial L/\partial e = 0, \qquad \partial L/\partial f = 0, \qquad \partial L/\partial g = 0.$$

i.e.,

$$\tfrac{1}{2}H\frac{\partial I}{\partial e} - m(e+f+g) - n(e-f-g) = 0,$$

$$\tfrac{1}{2}H\frac{\partial I}{\partial f} - m(e+f+g) - n(f-g-e) = 0,$$

$$\tfrac{1}{2}H\frac{\partial I}{\partial g} - m(e+f+g) - n(g-e-f) = 0.$$

In the case of a long cylindrical wire with axis along ox, we have $g = f$, and $\partial I/\partial g = \partial I/\partial f$, hence solving for e

$$ne = \tfrac{1}{2}\frac{m}{3m-n}H\frac{\partial I}{\partial e} - \tfrac{1}{2}\frac{m-n}{3m-n}H\frac{\partial I}{\partial f} = \tfrac{1}{2}\frac{m}{3m-n}H\left(\frac{\partial I}{\partial e} - \frac{m-n}{m}\frac{\partial I}{\partial f}\right). \quad . \quad (4).$$

Now if a tension δP per unit area be applied to the wire and produce an increase δI in the magnetisation and strains δe, $\delta f = \delta g$, then

$$\delta I = \frac{\partial I}{\partial e}\delta e + 2\frac{\partial I}{\partial f}\delta f.$$

But if the elastic properties of the material are not altered by magnetisation,

$$\delta f = -\tfrac{1}{2}\frac{m-n}{m}\,.\,\delta e,$$

therefore

$$\delta I = \left(\frac{\partial I}{\partial e} - \frac{m-n}{m}\frac{\partial I}{\partial f}\right)\delta e.$$

Hence (4) becomes

$$ne = \tfrac{1}{2}\frac{m}{3m-n}H\frac{\delta I}{\delta e},$$

therefore

$$e = \frac{1}{2E}H\frac{\delta I}{\delta e} = \tfrac{1}{2}H\frac{\delta I}{\delta P}.$$

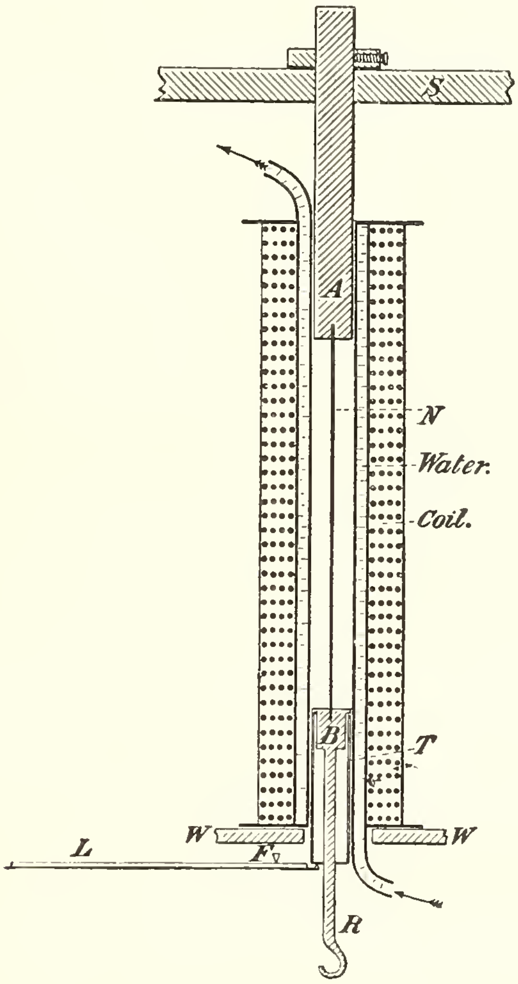
This strain will be the same at all points of the wire, which is supposed uniformly magnetised, and will therefore be that part of α which is due to these stresses.

Apparatus.

In the experiments nickel was used because the quantities to be measured are both greater and of a simpler nature than in the other magnetic metals. The specimen was an annealed wire of length 85·2 centims. and mean diameter 1·65 millims., containing about 98 per cent. of nickel and traces of iron and cobalt. This was obtained from Messrs. JOHNSON, MATTHEY and Co.

The magnetising coil was over a metre long, and consisted of seven layers of No. 18 copper wire wound on a hollow brass core provided with a water-jacket through which water could be made to flow steadily. The coil was mounted on a stand W (fig. 1) in a vertical position.

Fig. 1.



The ends of the nickel wire N were soldered into two brass pieces, the upper of which, A, was a long cylindrical bar, and the other, B, a short block of brass prolonged downwards by a tube T[*] closed at the lower end. Both bar and tube fitted loosely in the core of the coil, the bar projecting and being fixed to a rigid support S above the coil, and the tube projecting slightly from the coil below. A thin brass rod R was screwed into the block B, and passing downwards through an opening in the lower end of the tube T, was attached to a scalepan below.

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[*] It was at first intended to measure YOUNG'S Modulus for the nickel wire, a measurement for which the above apparatus was not very suitable, and which was moreover afterwards rendered unnecessary.

The method adopted for observing changes in the length of the nickel wire was essentially the same as has been used by several experimenters. At one end of a long light lever L, of wood, a sharp gun-metal point pressed upwards against the lower end of the tube T, and the fulcrum F consisted of two gun-metal points resting on two plates of glass fixed on a support which was rigidly connected with the upper support S; the connexion is not shown in the diagram (fig. 1). At the end of the other (longer) arm of the lever, a small metal plate was attached, at one point of which a slight depression was made; in this depression rested one of the three needle-point feet of a small light table on which a plane mirror was mounted. The two other feet rested on a fixed horizontal metallic support. Deflections of this mirror were observed by a telescope and vertical scale at a distance of about 3 metres.

Levers of various lengths were tried; the arms of the lever ultimately chosen were 3·275 centims. and 60·92 centims. long, measured from the line joining the fulcrum points to the point at one end, and the depression at the other, respectively. The distance of the moving foot of the mirror table from the line joining the two fixed feet was 8·97 millims. The magnifying power of this arrangement was 12,300.

The nickel wire was thus suspended inside but independently of the coil. The effect of any "suction" between the coil and the wire was, however, quite negligible, on account of the great rigidity of the support S, and because this support was rigidly connected with the fulcrum support of the lever, so that any displacement of the upper support involved a similar displacement of the fulcrum support, and therefore no *turning* of the lever. This was tested by observing the scale deflections caused by placing weights on the upper support S. Even if the wire had only one pole, the error due to this cause would be less than 0·1 per cent. of the deflection observed when the current was made.

The error due to the slight non-uniformity of the field of the coil towards the ends of the nickel wire was also of the same order.

The magnetising current was generally measured by a Kelvin graded galvanometer, standardised by electrolysis of copper, the smaller currents by a Kelvin centiampere balance.

For measuring the magnetisation, which was done in separate experiments, 600 turns of No. 40 double-silk covered and shellacked copper wire were wound in one layer near the middle of the nickel wire. These were connected to a ballistic galvanometer which was wound with wire calculated to give the greatest sensitiveness.* A long solenoid with secondary coil was used to standardize this galvanometer in the usual way.

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* See A. GRAY, "Absolute measurements in Electricity and Magnetism," vol. 2, Part II., p. 369.

Measurement of I *and* $\delta I/\delta P$.

The magnetisation was measured by observing the deflection of the galvanometer needle when the magnetising current was reversed. The sectional areas of the nickel wire and of the coil wound on it being known, and the galvanometer being frequently standardised, the induction in the wire, and hence the magnetisation, were calculated.

In order that equation (3) should hold, it was necessary that the nickel wire should be in the same magnetic state in the magnetisation and in the elongation experiments. Hence, both experiments were made with increasing reversals of magnetisation. Also, since during the reversals of magnetisation the magnetic stress is alternately applied and removed, the weight used in measuring $\delta I/\delta P$ was added and removed several times before readings were taken. An initial weight of 1 kilogram was always kept in the scalepan and the effect observed at several fields of adding a few kilograms, the magnetisation being measured before and after the additional load was applied.

An increase of tension always caused a diminution of magnetisation, which was not in general proportional to the weight added.* [Added May 15.—This depends on the field-strength. At low fields, within the range of tensions used in the present experiments, the effect of tension in reducing magnetisation diminishes slightly as the tension is increased, at stronger fields the opposite is th ecase; in other words, at low fields $\partial^2 I/\partial P^2$ is positive, at high fields negative. This may partly explain the fact observed by BIDWELL that at low fields increase of tension diminishes the magnetic contraction in nickel, at high fields increases it. For if part of the contraction is represented by

$$- e = \tfrac{1}{2} H \frac{\partial I}{P \partial},$$

then

$$\frac{\partial e}{\partial P} = - \tfrac{1}{2} H \frac{\partial^2 I}{\partial P^2},$$

which is negative at low, positive at high fields.] It could, however, be assumed that the change of magnetisation, divided by the increase of tension per unit area of section of the wire, gave the value of $\delta I/\delta P$ for the mean load. The curve of increasing reversals for the mean load was then determined.

Several loads were tried, but the effects of adding 2 and 7 kilograms respectively sufficiently show the nature of the results. Thus, the curves of increasing reversals of magnetisation, and the corresponding values of $\delta I/\delta P$, were determined with 2 and 4·5 kilograms in the scalepan, the total tensions being 2·4 and 4·9 kilograms.

Since the dimensional ratio of the nickel wire was about 500, the mean demagnetising force† was ·00018 I. This was never more than about 0·1 per cent. of the magnetising force due to the coil.

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[*] See EWING, 'Magnetic Induction in Iron and other Metals,' p. 196, 1893.

[†] DU BOIS, 'The Magnetic Circuit in Theory and Practice,' p. 41, 1896.

All ballistic measurements were repeated a number of times, and mean values taken, to eliminate, as far as possible, small errors of observation.

Measurement of Magnetic Change of Length.

It was necessary to determine the change of length of the nickel wire under tensions of 2·4 and 4·9 kilograms, for a series of increasing fields, the current being reversed a few times at each step.

Instead of doing this directly, by first demagnetising the wire and then applying the current, it was found more convenient to measure the temporary and residual changes of length separately.

The temporary change of length was determined by first making and reversing several times a measured current, and then observing the scale deflection caused by breaking the current. The reversed current was then made, the deflection observed on breaking it, and the mean of the two deflections taken. The wire always lengthened when the current was broken.

No complete hysteresis loops were obtained, but the opportunity was taken of noting how much of the residual contraction could be removed by applying a reversed field. Thus each time the current was broken a small reversed current was applied, causing an increase of length, and this current was gradually increased until the length reached a maximum, and at higher fields again diminished.

Next a series of residual contractions was determined, the wire being demagnetised by reversals before each reading and a current made for a short time, the scale reading being taken before the current was made and after it was broken.

The residual contraction was always found to be greater than the contraction which can be removed by applying an increasing reversed current. This has also been observed by Mr. NAGAOKA.[*]

As the magnetising field is increased both the residual and the "removable" contraction at first increase and then become nearly constant, the former being then about $2·5 \times 10^{-6}$ and the latter $1·9 \times 10^{6}$ of the length of the wire.

The reversed field corresponding to minimum contraction was about 16 C.G.S.

The temporary contraction was, however, still increasing in the highest fields employed, its value at $H = 350$ being about 33×10^{-6}, with a tension of 4·9 kilograms.

The curve representing the total contraction was obtained by adding the ordinates of the "temporary" and "residual" curves.[†]

The difference between the tensions 2·4 and 4·9 kilogs. weight was not sufficient to cause much difference in the curves. At the highest fields used the contractions were, however, rather greater with the greater tension.

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[*] 'Phil. Mag.,' Jan., 1894, p. 131.

[†] Since about a centimetre of the nickel wire at each end was soldered in the brass pieces A and B, the length of wire whose changes were measured was only 83·2 centims. This exposed length l was used in calculating α.

At low and moderate field-strengths the contraction is less, but at strong fields greater, than the value obtained by Mr. NAGAOKA for an ellipsoid of nickel.[*]

Water was kept flowing through the coil for a considerable time before readings were taken, and all temperature changes took place so slowly that their effects were easily distinguishable from the magnetic effect.

All the readings were repeated several times, and the points representing the results always lay very near the curve (fig. 3).

Final Results.

On the right-hand side of the equation (3) the third term is much greater than the other two. Hence it was not necessary to know E and θ with very great accuracy. The value of YOUNG's Modulus for a 98·1 per cent. nickel wire has recently been given by MEYER[†] as $21 \cdot 3 \times 10^{11}$ C.G.S. This value of E was used, and the rigidity was measured by observing the torsional oscillations of the wire, to which a cylindrical vibrator was attached. This gave $n = 7 \cdot 75 \times 10^{11}$ approximately. Hence $\theta = 1 \cdot 5$.

The greatest numerical value of $\frac{1}{2} \mathrm{H} (\delta \mathrm{I} / \delta \mathrm{P})$ obtained was about $8 \cdot 2 \times 10^{-6}$, while the greatest value of the first two terms in (3), representing the elongation due to MAXWELL's stresses, was but $0 \cdot 29 \times 10^{-6}$.

Tables I and II contain the values of H, I, the change $\delta \mathrm{I}$ of magnetisation caused by increasing the tension by $\delta \mathrm{P}$ per unit area of section, the values of $\delta l / l$ calculated from equation (3), and the observed total contraction $- \alpha$.

TABLE I.

Load = 2·4 kilogs. $\delta \mathrm{P} \times$ section of wire = 2 kilogs. Temperature = 6° C.

H.	I.	δI.	$\frac{\delta l}{l} . 10^6$ calculated.	$\alpha . 10^6$ observed.	$\left(\alpha - \frac{\delta l}{l}\right) 10^6$.	$\mathrm{I}^4 . 10^{-6}$.
7·49	31·0	− 1·6	− 0·063	− 0·1	− ·037	0·92
12·36	105	− 6·4	− 0·412	− 0·3	+ ·11	121·5
36·3	270	− 17·0	− 3·23	− 5·2	− 1·97	5316
64·3	332	− 15·3	− 5·15	− 11·35	− 6·2	12,140
85·5	365	− 13·4	− 6·00	− 15·05	− 9·05	17,750
107·5	389	− 13·0	− 7·30	− 18·35	− 11·05	22,890
159·0	428	− 9·7	− 8·07	− 23·6	− 15·53	33,550
212·0	452	− 5·0	− 5·45	− 27·4	− 21·95	41,730

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[*] 'Wied. Ann.,' vol. 53, p. 487, 1894.

[†] 'Wied. Ann.,' vol. 59, p. 668, 1896.

TABLE II.

Load = 4·9 kilogs. $\delta P \times$ section of wire = 7 kilogs. Temperature = 6° C.

H.	I.	∂I.	$\frac{\partial l}{l} \cdot 10^6$ calculated.	$\alpha \cdot 10^6$ observed.	$\left(a - \frac{\partial l}{l}\right) 10^6$.	$I^4 \cdot 10^{-6}$.
36·8	243	− 63·0	− 3·5	− 5·3	− 1·8	3490
65·2	308	− 60·0	− 5·9	− 11·5	− 5·6	9000
88·1	343	− 54·0	− 7·17	− 15·45	− 8·3	13,850
129·0	386	− 40·3	− 7·81	− 20·75	− 12·9	22,200
164·8	415	− 32·0	− 7·89	− 24·2	− 16·3	29,650
213·0	443	− 22·4	− 7·09	− 28·0	− 20·9	38,500
243·1	456	− 18·0	− 6·46	− 30·0	− 23·5	43,250
291·5	471	− 12·1	− 5·14	− 32·6	− 27·5	49,200
345·0	480	− 11·1	− 5·59	− 34·8	− 29·2	53,100

Fig. 2.

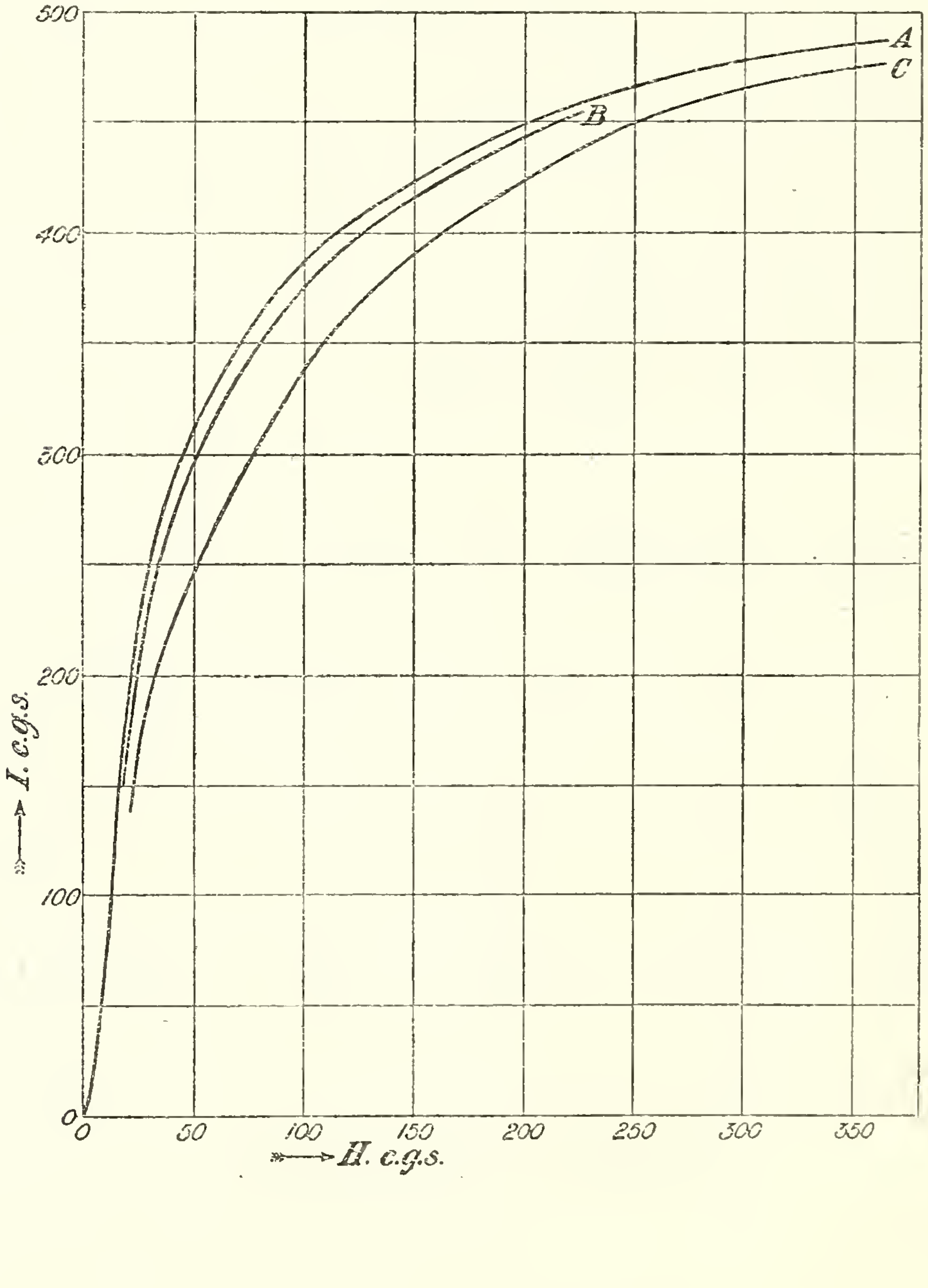


Fig. 3.

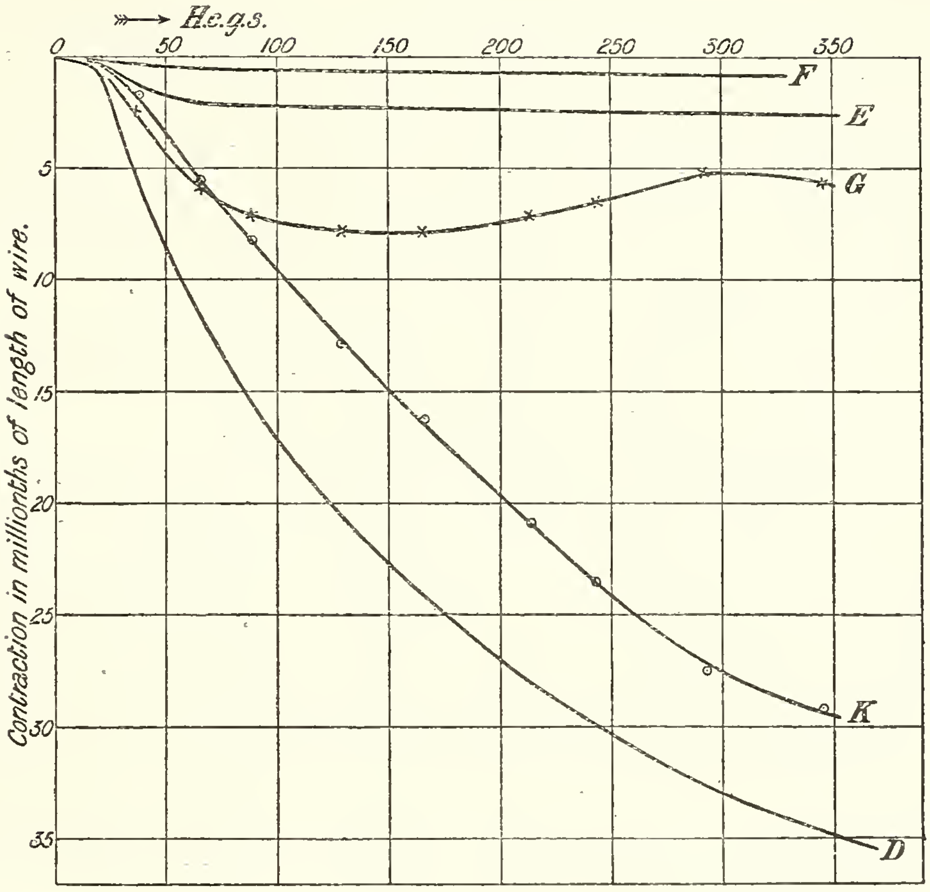
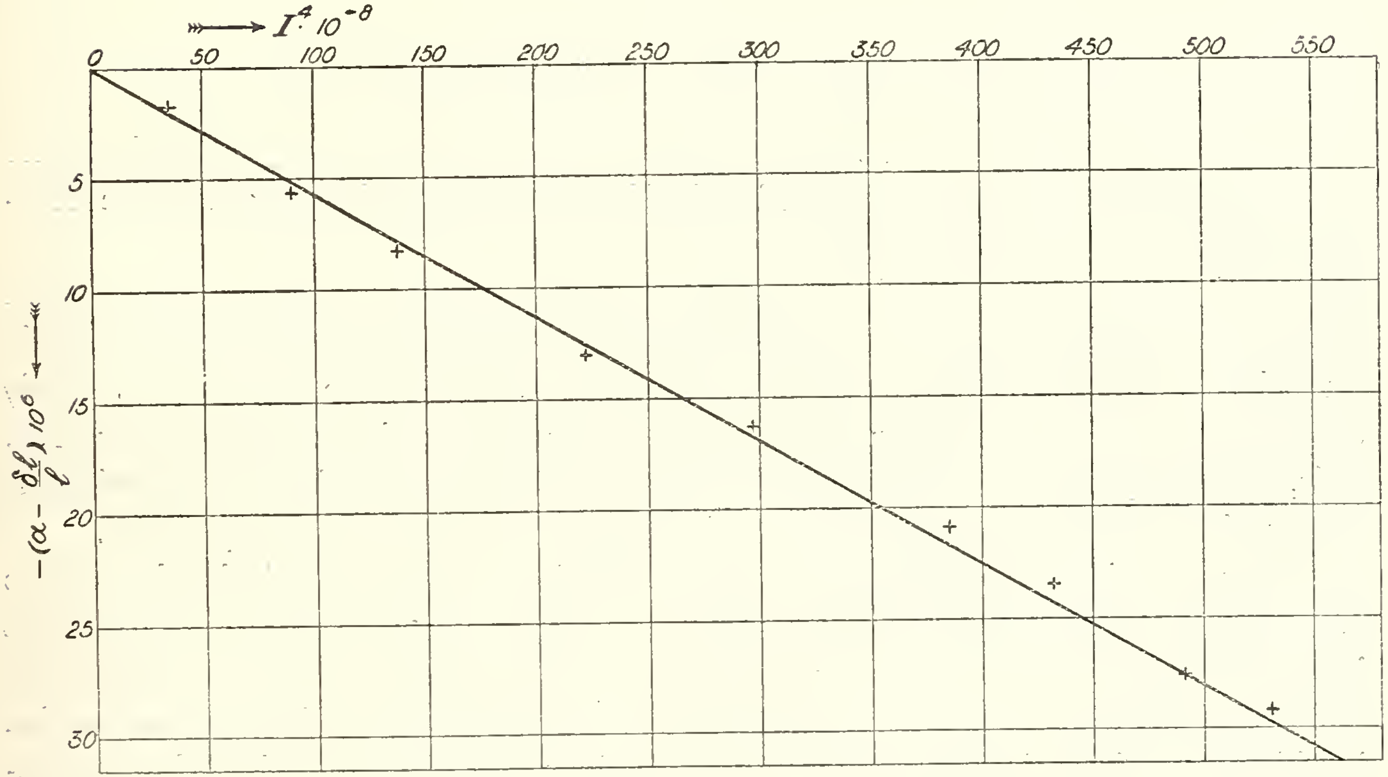


Fig. 4.



In fig. 2, Curve A is the curve of increasing reversals of magnetisation with a load of 1·4 kilogs. The difference of the ordinates of Curves A and B represents the diminution of magnetisation caused by adding two kilogs. to the load, and the difference of ordinates of A and C represents the effect of adding seven kilogs. to the load.

In fig. 3 curve D represents the observed total contraction $-\alpha$, curve E the residual contraction after the field H has been removed, F the least contraction attainable by reversing the current after the field H has been removed, G the value of $\delta l/l$ calculated from equation (3), and K the difference $\alpha - \delta l/l$, all as functions of the field H, the load being 4·9 kilogs. The curve K therefore represents the contraction in nickel corrected for the effects of known stresses.

In the last columns of Tables I and II, the corresponding values of I^4 are given. It will be seen that these numbers are approximately proportional to the numbers in the preceding column representing the values of $\alpha - \delta l/l$.

This is also shown in fig. 4, where the abscissæ of the points . . . + + + are proportional to I^4, and the ordinates to the corrected contraction $-(\alpha - \delta l/l)$ for the load 4·9 kilog. The points all lie, to within about 5 per cent., on a certain straight line passing through the origin. An error of 5 per cent. in the values of I^4 and $\delta I/\delta P$ might be caused by much smaller errors in the measurement of I. Especially was this the case with the other load 2·4 kilog., for the change of magnetisation δI in this case (Table I) was smaller, and therefore more difficult to measure accurately, though even in this case there is no regular deviation from proportionality between I^4 and $\alpha - \delta l/l$.

With the load 4·9 kilog., however, the change of length α observed in the nickel wire is closely represented by the equation

$$\alpha = cI^4 + \frac{4\pi}{3E} \cdot \frac{1+\theta}{1+2\theta} \cdot I^2 + \frac{HI}{2E(1+2\theta)} + \tfrac{1}{2}H\frac{\delta I}{\delta P},$$

where c has the value $-·056 \times 10^{-14}$ at the temperature 6° C., and where the second and third terms on the right-hand side are numerically very small in comparison with the first and fourth.

[Added May 15.—The result that the magnetic contraction in nickel, corrected in the manner described above for the effects of KIRCHHOFF's stresses, is under certain conditions approximately proportional to I^4, is at present to be regarded as purely empirical, and without further experiments it cannot be said to be generally true. It is, therefore, proposed to continue the investigation by repeating the experiments on the nickel wire under different conditions, especially as regards temperature.

It should be borne in mind that in the deduction of the theoretical value of the magnetic contraction, the material is supposed to be perfectly "soft," and no account is taken of hysteresis. Some experiments made by NAGAOKA on an ellipsoid of nickel ('Wied. Ann.,' 53, p. 496, 1894) seem to show, however, that the contraction in this metal depends only on the value of the magnetisation, being almost independent of the manner in which that value has been reached. It is, therefore, unlikely that any considerable discrepancy can arise in consequence of hysteresis.]

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IX. *On the Application of Harmonic Analysis to the Dynamical Theory of the Tides.*—Part I. *On* LAPLACE'S *"Oscillations of the First Species," and on the Dynamics of Ocean Currents.*

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Communicated by Professor G. H. DARWIN, *F.R.S.*

Received March 12,—Read April 8, 1897.

THE earliest attempt to subject the Theory of the Tides to a rigorous dynamical treatment was given by LAPLACE in the first and fourth books of the 'Mécanique Céleste.' The subject has since been treated by AIRY,[*] KELVIN,[†] DARWIN,[‡] LAMB,[§] and other writers, but with the exception of the extension of LAPLACE'S results to include the theory of the long-period tides, but little practical advance has been made with the subject, in spite of the enormous increase in the power of the mathematical resources at our disposal, and the problem has remained in very much the same condition as it was left by LAPLACE. This arises no doubt partly from the difficulties inherent to the subject, but partly from the form in which the theory was originally presented by LAPLACE in the 'Mécanique Céleste,' which has been described by AIRY as "perhaps on the whole more obscure than any other part of the same extent in that work." The obscurity complained of does not however seem to have been entirely removed by LAPLACE'S successors, and it was the fact that every presentment of the theory with which I was acquainted offered some points of difficulty, that in the first instance led me to take up the problem *ab initio*, partly with the purpose of allaying the doubts which had arisen in my own mind as to the validity of certain approximations employed by LAPLACE and adopted by his successors, and partly in the hope that I might be able to extend the results of LAPLACE to meet more fully the case presented by the circumstances actually existent in Nature.

Up to the present I have been unable to free the problem to any extent from the limitations which have been imposed by previous writers, and consequently it would be futile to claim that the results I am now able to put forward materially advance our knowledge of the tides as they actually exist; but I venture to hope that these results, as applied to the oscillations of an ideal ocean, considerably simpler in character than the actual ocean, may prove of some interest from the point of view of pure hydrodynamical theory.

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[*] 'Encyc. Metropolitana'; Art., "Tides and Waves," Section III.

[†] 'Phil. Mag.,' 1875, vol. 50.

[‡] 'Encyc. Britannica' (9th edition); Art., "Tides."

[§] 'Hydrodynamics,' chapter viii.

In §§ 1–4 I have devoted considerable space to the formation of the dynamical equations. The equations obtained agree with those used by LAPLACE, and consequently it may be thought that I have been unnecessarily diffuse over this part of the subject. My apology is that the questionable, if not erroneous, reasoning which has often been assigned for the various approximations introduced seemed to me to warrant a very minute examination of the formation of these equations. An analytical treatment, such as that I have used, seems to me to be the only safe method of procedure to ensure that the approximations do not involve the neglect of any terms which may be of equal importance with those retained, many of which are extremely small. The method adopted follows LAPLACE in so far as it consists of a transformation of the general equations of oscillation of a rotating fluid. I trust however that these general equations in the form I have used, which seems to be the simplest form to which they can be reduced, may be found less "repulsive" than those employed by LAPLACE.

§ 5 deals with the integration of these equations. The forms of solution discussed in the present paper are those which are symmetrical with respect to the axis of rotation. The types of oscillation represented by these solutions have been named by LAPLACE, "Oscillations of the First Species," but he omitted to discuss them in detail on the grounds that the oscillations of such character, which might be expected to exist in Nature, would be modified to such an extent by friction that they would be far better represented by the old "equilibrium theory," than by a dynamical theory which failed to take due account of the action of friction. The tides in question will be of long period, the shortest of the periods being half a lunar month in duration, but Professor DARWIN was, I believe, the first to call attention to the fact that this length of period will hardly be sufficiently great to render the effects of friction of such paramount importance, and hence he added to the work of LAPLACE a discussion of the long-period tides when not subject to frictional influences. I have recently attempted to estimate the effects of friction on the tidal oscillations of the ocean,* and the results at which I have arrived fully confirm the view of Professor DARWIN as to the small influence of friction on the lunar-fortnightly tides, and render it highly probable that the effects will be almost equally slight on the solar long-period tides.

The method of integration I have employed differs from that used by DARWIN, my aim having been to express the results by means of series of zonal harmonics instead of by the power-series obtained by him. The advantages of this are two-fold; firstly, it allows of our including in our analysis the effects due to the gravitational attraction of the water ; and secondly, the convergence of the series obtained will be much more rapid. The latter circumstance is of particular value, as it has enabled me to treat with considerable success the problem of the free oscillations of the ocean.

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* In a paper read before the London Math. Soc., December 10th, 1896.

The general problem of the small oscillations of a rotating system possessing a finite number of degrees of freedom has been discussed by THOMSON and TAIT ;[*] but the extension to meet the case where the number of degrees of freedom is infinite involves analytical considerations of some delicacy. As a rule, the transition from the case of a system with finite freedom to that of a system with infinite freedom is effected by the employment of "normal coordinates,"[†] and the chief difficulty in the solution of problems relating to the vibrations of the latter class of system consists in the discovery of these coordinates. The researches of THOMSON and TAIT just mentioned shew however that in a rotating system these normal coordinates do not exist, and hence that the methods ordinarily employed to deal with the oscillations of a system about a state of equilibrium will no longer suffice for the treatment of our problem. In most "gyrostatic" problems which have been solved hitherto,[‡] the solution has been obtained by means of a system of quasi-normal coordinates. When such coordinates exist, only a finite number of oscillations of certain particular types are possible, and, by constraining the system to vibrate in one of these types, we may treat it in the same manner as a system with a finite number of degrees of freedom. The period-equation for the free oscillations of an assumed type will then only possess a finite number of roots, and will consequently be an algebraic equation usually most readily obtained in a determinantal form. It is shewn at the end of § 5 that the coordinates we have used possess this property when the depth of the ocean follows certain restricted laws ; but in general no such quasi-normal coordinates exist, and whatever coordinates be employed, the displacements in any of the fundamental modes of vibration can only be expressed by means of an infinite number of such coordinates. The most advantageous choice of coordinates will then be that which leads to most rapidly converging series.

As however the oscillations of an assumed type can only be expressed by an infinite series of coordinates, it follows that an infinite number of oscillations of any assumed type must be possible, and that consequently the period-equation for oscillations of this type will have an infinite number of roots and will therefore be transcendental instead of algebraic in character. It is possible that the transition from systems with finite freedom to systems with infinite freedom may be treated with advantage by the employment of determinants of infinite order (as a means of expressing the transcendental period-equation), after the manner introduced into analysis by

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[*] 'Natural Philosophy,' Part I., § 345.

[†] RAYLEIGH, 'Theory of Sound,' vol. 1, § 87.

[‡] *Cf.* POINCARÉ, 'Acta Mathematica,' vol. 7 ; BRYAN, 'Phil. Trans.,' 1889.

G. W. HILL, in his 'Researches on the Lunar Theory;'* but in the present instance we are able to avoid the difficulties involved in the use of these infinite determinants, in that the forms of determinant which occur are those which are associated with continued fractions.

§ 6 deals with the analytical discussion of the deduction of the period-equation. The method is based on a paper by Lord KELVIN,† in which the author defends the procedure of LAPLACE against certain allegations to which it had been subjected by AIRY, but I have endeavoured to present the arguments in a somewhat different light, so as to bring out more clearly the analogy between our problem and the general problem of vibrating systems with finite freedom.

In §§ 7–10 I have given illustrations of the method of solving the period-equation numerically, and of the subsequent determination of the type of motion for the different fundamental modes. As the ground covered in these sections is almost entirely new, I have devoted considerable time and labour to the arithmetical determination of the periods and types of the principal oscillations for a system comparable with the earth in magnitude. The results are tabulated in these sections.

§ 11 deals briefly with the forced tides of long period due to the moon in an ocean of uniform depth. The results agree with those previously obtained by other methods, but differ from them in analytical form. In § 12 I have given illustrations of a means of extending the method of numerical computation to cases where the law of depth is less restricted in character.

The consideration of forced tides of very long period, dealt with in § 13, points to the existence of free oscillations of infinitely long period. This, I believe, was first noted by Professor LAMB,‡ but the application of the dynamical equations for the tides to the treatment of these free oscillations has not been previously carried out. The types of motion in question appear to be of considerable importance, as they throw light on a phenomenon which in the past has been the subject of considerable controversy. The difficulties which have been met with in attempts to account for the existence of ocean currents all seem to me to arise from an over-estimate of the effects of viscosity on the motion of the sea. The large-scale ocean currents have been attributed by Sir JOHN HERSCHEL§ and others entirely to the influence of the "trade" and other prevailing winds, which give rise to slow steady motions which, in the absence of friction, would remain permanent even were the originating cause entirely to cease. The difficulty in accepting this view arises from the assumption that such currents would succumb to the influence of frictional resistances in the course of a few days.* If this assumption be correct it will of course be necessary to invoke some more constant cause than the fickle winds in explanation of ocean currents, but unfortunately the causes put forward by the chief opponents of the wind theory, namely, the differences of density arising from differences of temperature, salinity, &c., though no doubt satisfying the criterion of being more constant in their action, seem to be equally ineffective in maintaining the currents against such large resistances as would be required to destroy the currents due to the winds in a few days. If, on the other hand, the period of subsidence of the free current-motions is to be reckoned rather by years, these motions could not fail to be excited and maintained by such causes as the winds even against the action of friction.

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* 'Acta Mathematica,' vol. 8.

† 'Phil. Mag.,' 1875, p. 227.

‡ 'Hydrodynamics,' § 198.

§ 'Physical Geography,' §§ 57–60.

In § 14 I have dealt with the dynamics of ocean currents on the supposition that they are of the nature of free steady motions (probably maintained by a variety of causes), and that the influences of viscosity are extremely small. A remarkable result is the extremely restricted character of the possible forms of steady motion as contrasted with the case where the ocean covers a non-rotating globe, in which latter case the possible forms of steady motion are to a large extent arbitrary. It is found that if the density of the water is uniform, the only forms of steady motion possible when the depth depends on the latitude alone are those in which the water always moves along parallels of latitude, while in general the paths of the fluid particles coincide with certain lines depending only on the distribution of land and water and on the configuration of the ocean bed. The equation by which these lines are defined is of an extremely simple character, and from it we could at once trace out the forms of the stream-lines on a chart if we had a sufficient knowledge of the configuration of the ocean bed. The equator will always be one of these stream-lines, and herein we seem to have the explanation of the fact that the ocean-currents always tend to set along the equator, but in other respects it is shewn that the effects of variations of density will seriously interfere with the simple laws which must hold so long as the density is uniform.

The importance of the earth's rotation in influencing ocean-currents has long been recognised by physicists, but I am not aware that any previous attempt has been made to investigate this influence mathematically. The numerical results obtained in § 15 are interesting, as showing how a cause, which on a non-rotating globe could not give rise to any appreciable currents, may be rendered highly effective in maintaining currents as a consequence of the rotation of the earth.

In attempting to account for ocean currents, the real question at issue is: How far are the suggested causes capable of maintaining currents *against the action of friction?* To answer this question an investigation, either mathematical or experimental, as to the effects of friction is essential. Such an investigation I have endeavoured to supply in another paper,[*] but mathematical difficulties have compelled me, in treating of friction, to omit from consideration the important influences due to the rotation. We have already called attention to the fact that the free steady motions on a non-rotating globe are far less restricted in character than those on a rotating globe, while, in that the latter essentially violate what appears to be a necessary condition when the water is viscous, namely, that there can be no slipping at the bottom, it seems to me to be probable that even the limited forms of steady motion here dealt with would be no longer possible if the water were viscous, but that, if they were started by any means, they would at once give place to periodic motions of comparatively short period.[†] This conclusion has been forced on me by the apparent impossibility of satisfying the equations of motion of a viscous ocean on a rotating globe by means of slowly declining current-motions. If such should be the case, it follows that no stable currents can exist without variations in the density of the water. As however I have not as yet been able to support this view by anything approaching a rigorous mathematical treatment, the question must for the present remain open.

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* MAURY, 'Physical Geography of the Sea,' § 93.

§ 1. *Differential Equations for the Vibration of a Rotating Mass of Liquid.*

Suppose we are dealing with the small oscillations of a mass of liquid about a state of steady motion consisting of a rotation as a rigid body with angular velocity ω about a certain axis.

Take this axis as axis of z, and refer to a set of rectangular axes rotating about it with uniform angular velocity ω. Then, in the steady motion supposed, the fluid will have no motion relatively to these axes.

Let u, v, w denote the relative velocity-components at the point x, y, z due to the small oscillations. The actual velocity-components parallel to the instantaneous positions of the moving axes will then be

$$u - \omega y, \quad v + \omega x, \quad w,$$

and, therefore, if we suppose the amplitude of the vibrations sufficiently small to allow of our neglecting squares and products of the small quantities u, v, w, the differential equations of motion of the liquid may be written in the form[‡]

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[*] *Loc. cit., ante.*

[†] The condition that there can be no slipping at the bottom will reduce the number of degrees of freedom of the system, and hence we may anticipate that certain types of motion which were possible before this condition was imposed will no longer exist afterwards.

[‡] BASSET, 'Hydrodynamics,' vol. 1, p. 22.

$$\begin{aligned}
\frac{\partial u}{\partial t} - \omega\,(v + \omega x) - \omega v &= \frac{\partial}{\partial x}\,(\mathrm{V}' - p/\rho), \\
\frac{\partial v}{\partial t} + \omega\,(u - \omega y) + \omega u &= \frac{\partial}{\partial y}\,(\mathrm{V}' - p/\rho), \\
\frac{\partial w}{\partial t} \qquad\qquad\qquad &= \frac{\partial}{\partial z}\,(\mathrm{V}' - p/\rho),
\end{aligned}$$

where V′ denotes the potential of the bodily forces acting on the liquid, p the fluid pressure, and ρ the density.

If now we put

$$\psi = \mathrm{V}' - p/\rho + \tfrac{1}{2}\omega^2\,(x^2 + y^2) + \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

the above equations reduce to

$$\left.\begin{aligned}
\frac{\partial u}{\partial t} - 2\omega v &= \frac{\partial \psi}{\partial x} \\
\frac{\partial v}{\partial t} + 2\omega u &= \frac{\partial \psi}{\partial y} \\
\frac{\partial w}{\partial t} \qquad\quad &= \frac{\partial \psi}{\partial z}
\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2),$$

while the incompressibility of the liquid is expressed by the additional equation

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3).$$

These equations, originally given by POINCARÉ,[*] suffice, in conjunction with certain conditions which must hold at the boundary, for the determination of the four functions u, v, w, ψ. They are perhaps the simplest equations of which to make use when dealing with the oscillations of a mass of liquid of finite extent in three dimensions, and, for this purpose, they were first solved by POINCARÉ in a form adapted for satisfying boundary-conditions at an ellipsoidal surface, while additional applications have been considered by BRYAN,[†] LOVE,[‡] and myself.[§] The possibility of solution in each of these cases however turns on the fact that it only required to satisfy boundary-conditions at a single ellipsoidal or spheroidal surface, whereas, in the problem presented by the tides, it is necessary to satisfy conditions at two surfaces, namely, the ocean bed and the free surface of the ocean.

There is, however, a feature attached to this problem which enables us to surmount the difficulties arising from this cause; the fluid which constitutes the ocean may be regarded as a thin layer distributed over an approximately spherical surface, a circumstance which enables us to reduce the number of our independent variables and to treat the problem as a two-dimensional one.

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[*] 'Acta Mathematica,' vol. 7, p. 356.

[†] 'Phil. Trans.,' 1889.

[‡] 'Proc. Lon. Math. Soc.,' vol. 19.

[§] 'Phil. Trans.,' 1895.

Before proceeding to the transformation of our equations, let us examine them in the form in which they are given above. If we suppose the system is executing a simple harmonic vibration in period $2\pi/\lambda$, we may put u, v, w, ψ each proportional to $e^{i\lambda t}$, and therefore replace $\partial u/\partial t$, &c., by $i\lambda u$, &c. Thus the equations (2) give

$$\begin{aligned} i\lambda u - 2\omega v &= \frac{\partial\psi}{\partial x}, \\ i\lambda v + 2\omega u &= \frac{\partial\psi}{\partial y}, \\ i\lambda w \quad &= \frac{\partial\psi}{\partial z}. \end{aligned}$$

Now in an important class of oscillations, viz., the tides of long period, the value of λ will be small compared with that of ω; while for another class of motions, viz., the steady ocean-currents, we must suppose λ absolutely zero. In these cases, if we retain only the most important terms, the equations of motion take the approximate form

$$-2\omega v = \frac{\partial\psi}{\partial x}, \qquad 2\omega u = \frac{\partial\psi}{\partial y}, \qquad 0 = \frac{\partial\psi}{\partial z}.$$

Hence, applying the operators $\partial/\partial z$ to the first two, and making use of the third, we find

$$\partial u/\partial z = 0, \qquad \partial v/\partial z = 0.$$

Likewise also from the equation of continuity,

$$\frac{\partial w}{\partial z} = -\frac{\partial u}{\partial x} - \frac{\partial v}{\partial y} = -\frac{1}{2\omega}\left(\frac{\partial^2\psi}{\partial x\,\partial y} - \frac{\partial^2\psi}{\partial y\,\partial x}\right) = 0.$$

From this we see that in the case of tides of very long period the velocity of the fluid particles is approximately the same at all points in the same line parallel to the polar axis, while in the case of the ocean-currents this is rigorously the case.

Now in order to effect the transformation of the equations of motion, it has been assumed by LAPLACE and his followers that, on the analogy of "long waves" when there is no rotation, all fluid particles which are at one instant in a vertical line will remain in such a line. This assumption appears to require some modification in the case of our rotating system. We shall see hereafter however that the assumption in question will not lead to appreciable error, provided that the depth of the water is small in comparison with the radius of the solid globe on which it resides, a hypothesis which will certainly be applicable in the case of the earth.

§ 2. *The Boundary-conditions.*

Before proceeding with the approximations which we propose to employ hereafter, let us examine the boundary-conditions to which the functions u, v, w, ψ are subject in the general case.

Suppose the fluid resides on the surface of a solid nucleus which is constrained to rotate with uniform angular velocity ω about the axis of z. We introduce this constraint so as to avoid the complications resulting from the reactions of the fluid motion on that of the nucleus. Since in the case of the earth the mass of the ocean is exceedingly small compared with that of the solid parts, such reactions would be very minute, while for most of the more important types of oscillation they would not exist at all. In such types the problem is not affected by the introduction of the constraints. The boundaries of the ocean where it is in contact with the solid nucleus may then be regarded as fixed relatively to the moving axes Ox, Oy, Oz, and the condition to be satisfied at these boundaries is that there is no flow of fluid across them. Denoting by l, m, n the direction-cosines of the normal to the surface, this condition is expressed analytically by the equation

$$[lu + mv + nw] = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

Next, let us examine the boundary-conditions at the free surface. Let l, m, n denote the direction-cosines of the normal to this surface in its undisturbed position, and let ζ be the distance between the displaced surface and the mean surface measured along the normal to the latter. Then we may equate the velocity at the mean surface in the direction of this normal to the rate at which ζ increases; thus at the undisturbed surface we have

$$[lu + mv + nw] = \partial\zeta/\partial t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5).$$

Lastly, we must express the condition that the pressure at the actual free surface is zero (or constant). Now if dn' denote an element of the normal to the undisturbed surface, and $\bar{p}$, $\overline{\dfrac{\partial p}{\partial n'}}$ denote the values at this surface of the pressure and its rate of increase along the normal, the pressure at the actual surface is

$$\bar{p} + \zeta\overline{\frac{\partial p}{\partial n'}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6),$$

and this we have seen is to be equated to a constant.

But by definition of ψ we have

$$
\begin{aligned}
p/\rho &= \text{const} + \mathrm{V}' + \tfrac{1}{2}\omega^2(x^2+y^2) - \psi \\
&= \text{const} + \mathrm{V}'_0 + v' + \upsilon + \tfrac{1}{2}\omega^2(x^2+y^2) - \psi \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7),
\end{aligned}
$$

where V'_0 denotes the potential at x, y, z in the steady motion, v' the potential due to the attraction of the layer of fluid contained between the actual free surface and its mean position, and υ the disturbing potential, which may be regarded as due to some external attracting system.

Since in (6) $\overline{\partial p}/\partial n'$ is already associated with the small factor ζ, in calculating $\overline{\partial p}/\partial n'$ we may omit all small quantities of the order ζ, and thus replace this expression by its value in the steady motion. But from (7) we have in this case

$$p/\rho = \text{const} + \mathrm{V}'_0 + \tfrac{1}{2}\omega^2(x^2+y^2),$$

whence

$$\frac{1}{\rho}\frac{\overline{\partial p}}{\partial n'} = \frac{\partial}{\partial n'}\{\mathrm{V}'_0 + \tfrac{1}{2}\omega^2(x^2+y^2)\}.$$

Now, since the free surface of the ocean must be an equipotential surface, the resultant of gravitation, including centrifugal force, must be perpendicular to this surface. Denoting by g its value, we have

$$g = -\frac{\partial}{\partial n'}\{\mathrm{V}'_0 + \tfrac{1}{2}\omega^2(x^2+y^2)\},$$

and therefore

$$\frac{1}{\rho}\frac{\overline{\partial p}}{\partial n'} = -g \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8).$$

Introducing the values of $\bar{p}$, $\dfrac{\overline{\partial p}}{\partial n'}$ from (7), (8) into the expression (6), and equating the latter to a constant, we find

$$[\mathrm{V}'_0 + v' + \upsilon + \tfrac{1}{2}\omega^2(x^2+y^2) - \psi] - g\zeta = \text{const},$$

or, on equating periodic parts to zero,

$$\bar{\psi} = \bar{v}' - g\zeta + \bar{\upsilon} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9),$$

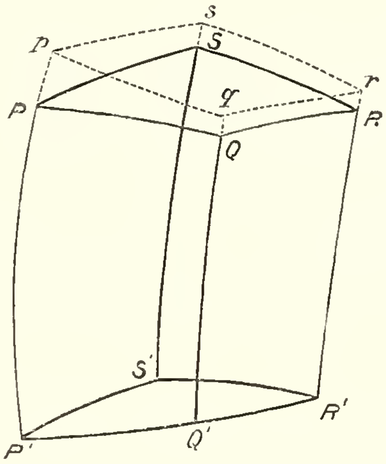
where the bars are used to denote surface-values at the undisturbed free surface.

§ 3. *Transformation of the Equation of Continuity.*

We proceed now to the transformation of our equations into a form analogous to that used by LAPLACE, dealing first with the equation of continuity.

Let us refer to a system of orthogonal curvilinear coordinates α, β, γ, and suppose that the undisturbed surface of the ocean coincides with one of the surfaces $\gamma=\text{const.}$, say $\gamma = \gamma_0$.

On the surface $\gamma = \gamma_0$ take a small parallelogram PQRS, bounded by curves of the systems $\alpha = \text{const}$, $\beta = \text{const}$.



Through the sides of this parallelogram draw the surfaces $\alpha = \text{const}$, $\beta = \text{const}$, to meet the inner surface of the ocean in the quadrilateral P′Q′R′S′ and the distorted free surface in *pqrs*.

The surfaces $\alpha = \text{const}$, $\beta = \text{const}$, are, of course, supposed to be in rotation with angular velocity ω, in common with the axes Ox, Oy, Oz. Let U, V, W denote the relative velocity-components at the point (α, β, γ) parallel to the normals to the surfaces of reference and in the directions in which α, β, γ respectively increase, and let $\gamma = \gamma_1$, where γ_1 may be regarded as a function of α, β, be the equation to the surface of the solid earth.

Let h_1, h_2, h_3 be parameters associated with our orthogonal system of coordinates, such that the line-element ds is given by

$$ds^2 = d\alpha^2/h_1^2 + d\beta^2/h_2^2 + d\gamma^2/h_3^2.$$

Then the volume of liquid which flows in a unit of time across the face $\alpha = \text{const}$ of an elementary parallelopiped whose adjacent edges are $\delta\alpha/h_1$, $\delta\beta/h_2$, $\delta\gamma/h_3$ is

$$\text{U}\,\frac{\delta\beta}{h_2}\,\frac{\delta\gamma}{h_3}.$$

But if in the above figure we suppose that α, β, γ_0 are the coordinates of P, and that PQ $= \delta\beta/h_2$, PS $= \delta\alpha/h_1$, the total flow of liquid across the face PP′Q′Q will be found by integrating the above expression with respect to γ between the limits $\gamma = \gamma_1$, $\gamma = \gamma_0$.

Thus, the rate at which liquid is entering the elementary volume PR′ across the face PQ′ is expressed by

$$\delta\beta \int_{\gamma_1}^{\gamma_0} (\mathrm{U}/h_2 h_3)\, d\gamma.$$

If in this expression we change α into $\alpha + \delta\alpha$, we shall obtain the rate at which fluid is flowing in the positive direction across the face SR′; therefore, the rate at which fluid is leaving the element across the face SR′ is expressed by

$$\delta\beta \int_{\gamma_1}^{\gamma_0} (\mathrm{U}/h_2 h_3)\, d\gamma + \delta\alpha\, \delta\beta \frac{\partial}{\partial\alpha} \left\{ \int_{\gamma_1}^{\gamma_0} (\mathrm{U}/h_2 h_3)\, d\gamma \right\}.$$

In like manner, the rate at which fluid enters across the face PS′ is

$$\delta\alpha \int_{\gamma_1}^{\gamma_0} (\mathrm{V}/h_3 h_1)\, d\gamma,$$

and that at which it escapes across the face QR′ is

$$\delta\alpha \int_{\gamma_1}^{\gamma_0} (\mathrm{V}/h_3 h_1)\, d\gamma + \delta\alpha\, \delta\beta \frac{\partial}{\partial\beta} \left\{ \int_{\gamma_1}^{\gamma_0} (\mathrm{V}/h_3 h_1)\, d\gamma \right\}.$$

Lastly, in virtue of the boundary-equation (4), which holds at the surface P′Q′R′S′, the rate at which fluid enters over this surface is zero, while in virtue of (5), which holds at the surface PQRS, the rate at which fluid escapes over the latter surface is expressed by

$$\frac{\delta\alpha}{h_1} \frac{\delta\beta}{h_2} \frac{\partial\zeta}{\partial t}.$$

Now the total amount of liquid contained within the elementary volume under consideration is constant, and therefore, if we equate to zero the sum of the rates at which fluid is entering over all the six faces, we obtain the equation of continuity in the form

$$- \delta\alpha\, \delta\beta \frac{\partial}{\partial\alpha} \left\{ \int_{\gamma_1}^{\gamma_0} (\mathrm{U}/h_2 h_3)\, d\gamma \right\} - \delta\alpha\, \delta\beta \frac{\partial}{\partial\beta} \left\{ \int_{\gamma_1}^{\gamma_0} (\mathrm{V}/h_3 h_1)\, d\gamma \right\} - \frac{\delta\alpha}{h_1} \frac{\delta\beta}{h_2} \frac{\partial\zeta}{\partial t} = 0,$$

or

$$\frac{\partial\zeta}{\partial t} = - h_1 h_2 \left[\frac{\partial}{\partial\alpha} \left\{ \int_{\gamma_1}^{\gamma_0} (\mathrm{U}/h_2 h_3)\, d\gamma \right\} + \frac{\partial}{\partial\beta} \left\{ \int_{\gamma_1}^{\gamma_0} (\mathrm{V}/h_3 h_1)\, d\gamma \right\} \right] \quad . \quad . \quad (10).$$

So far no approximation has been made other than that involved in supposing the vibrations small. If we now suppose that the depth of the water is small, so that $\gamma_0 - \gamma_1$ is a small quantity, the above equation admits of considerable simplification. Using square brackets to denote values at the mean surface $\gamma = \gamma_0$, we have, by TAYLOR'S Theorem,

$$U/h_2h_3 = [U/h_2h_3] + (\gamma - \gamma_0)\left[\frac{\partial}{\partial\gamma}(U/h_2h_3)\right] + \ldots,$$

whence

$$\int_{\gamma_1}^{\gamma_0}(U/h_2h_3)\,d\gamma = [U/h_2h_3](\gamma_0 - \gamma_1) - \tfrac{1}{2}(\gamma_0 - \gamma_1)^2\left[\frac{\partial}{\partial\gamma}(U/h_2h_3)\right] + \ldots.$$

Now, if $\gamma_0 - \gamma_1$ be small as supposed above,* even though $\frac{\partial}{\partial\gamma}(U/h_2h_3)$ is finite, we may omit all the terms on the right except the first. This amounts to supposing that the horizontal velocity is sensibly uniform throughout the depth, not on account of the small value of its rate of variation, but on account of the small distance through which this variation can take effect, a supposition which is not inconsistent with the results of § 1. Hence, on neglecting small terms of the order $(\gamma_0 - \gamma_1)^2$, we have

$$\int_{\gamma_1}^{\gamma_0}(U/h_2h_3)\,d\gamma = [U/h_2h_3](\gamma_0 - \gamma_1),$$

and, in like manner,

$$\int_{\gamma_1}^{\gamma_0}(V/h_2h_3)\,d\gamma = [V/h_3h_1](\gamma_0 - \gamma_1).$$

Let h denote the depth of the ocean at the point (α, β). Then, provided h be small in comparison with the radii of curvature of normal sections of the surfaces $\alpha =$ const, $\beta =$ const, $\gamma =$ const, we may put

$$\frac{\gamma_0 - \gamma_1}{[h_3]} = h,$$

with errors of the order of the square of the ratio of h to these radii of curvature; and therefore

$$\int_{\gamma_1}^{\gamma_0}(U/h_2h_3)\,d\gamma = h\,[U/h_2],$$

$$\int_{\gamma_1}^{\gamma_0}(V/h_3h_1)\,d\gamma = h\,[V/h_1].$$

Substituting these values in (10), we find

$$\frac{\partial\zeta}{\partial t} = -\,\bar{h}_1\bar{h}_2\left[\frac{\partial}{\partial\alpha}\left(\frac{\bar{U}h}{\bar{h}_2}\right) + \frac{\partial}{\partial\beta}\left(\frac{\bar{V}h}{\bar{h}_1}\right)\right] \quad \ldots\ldots \quad (11),$$

where we have now used bars to denote surface values.

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* The standard of comparison is considered in the next section.

If we suppose that the free surface of the ocean is a spheroid of revolution about the axis Oz, it will be convenient to refer to a system of spheroidal coordinates μ, ϕ, ν related to x, y, z by the equations

$$\begin{aligned} x &= c\sqrt{(1+\nu^2)}\sqrt{(1-\mu^2)}\cos\phi, \\ y &= c\sqrt{(1+\nu^2)}\sqrt{(1-\mu^2)}\sin\phi, \\ z &= c\nu\mu. \end{aligned}$$

The line-element ds for this system of coordinates is given by

$$ds^2 = \frac{c^2(\nu^2+\mu^2)}{1-\mu^2}\,d\mu^2 + c^2(1+\nu^2)(1-\mu^2)\,d\phi^2 + \frac{c^2(\nu^2+\mu^2)}{1+\nu^2}\,d\nu^2\,;$$

whence, if we identify μ, ϕ, ν with α, β, γ respectively, we have

$$\frac{1}{h_1} = \frac{c\sqrt{(\nu^2+\mu^2)}}{\sqrt{(1-\mu^2}}\,, \qquad \frac{1}{h_2} = c\sqrt{(1+\nu^2)}\sqrt{(1-\mu^2)}, \qquad \frac{1}{h_3} = \frac{c\sqrt{(\nu^2+\mu^2)}}{\sqrt{(1+\nu^2)}},$$

and, supposing that $\nu = \nu_0$ is the equation to the free surface, the equation (11) becomes

$$\frac{\partial\zeta}{\partial t} = -\frac{1}{c\sqrt{(\mu^2+\nu_0^2)}}\frac{\partial}{\partial\mu}\left\{\sqrt{(1-\mu^2)}\,h\,\mathrm{U}\right\} - \frac{1}{c\sqrt{(\nu_0^2+1)}}\frac{\partial}{\partial\phi}\left\{\frac{h\,\mathrm{V}}{\sqrt{(1-\mu^2)}}\right\}.$$

We have already neglected on the right small terms of the order h compared with those retained; we now propose to make the further hypothesis that the spheroidal surface of the ocean is of small ellipticity ϵ. In this case c will be small and ν_0 large, in such a manner however that $c\nu_0$ is finite and equal to the polar radius a; further $1/\nu_0^2$ will be approximately equal to 2ϵ. Hence we find

$$\frac{\partial\zeta}{\partial t} = -\frac{1}{a}\left[\frac{\partial}{\partial\mu}\left\{\sqrt{(1-\mu^2)}\,h\,\mathrm{U}\right\} + \frac{\partial}{\partial\phi}\left\{\frac{h\,\mathrm{V}}{\sqrt{(1-\mu^2)}}\right\}\right] \quad . \quad . \quad . \quad (12),$$

where the terms omitted on the right are of order h and of order ϵ compared with those retained.

§ 4. *Transformation of the Dynamical Equations.*

Let θ denote the inclination to the axis of z of the normal to the surface $\nu =$ const, through any point; then the direction-cosines of this normal will be

$$\sin\theta\cos\phi, \qquad \sin\theta\sin\phi, \qquad \cos\theta\,;$$

and the direction-cosines of the normals to the surfaces $\mu = \text{const}$, $\phi = \text{const}$, will be

$$\begin{array}{ccc} -\cos\theta\cos\phi, & -\cos\theta\sin\phi, & \sin\theta, \\ -\sin\phi, & \cos\phi, & 0, \end{array}$$

respectively. Hence we have

$$\begin{aligned} U &= -(u\cos\phi + v\sin\phi)\cos\theta + w\sin\theta, \\ V &= v\cos\phi - u\sin\phi, \\ W &= (u\cos\phi + v\sin\phi)\sin\theta + w\cos\theta, \end{aligned}$$

from which we obtain

$$-U\cos\theta + W\sin\theta = u\cos\phi + v\sin\phi.$$

Again

$$h_1\frac{\partial\psi}{\partial\mu} = -\frac{\partial\psi}{\partial x}\cos\phi\cos\theta - \frac{\partial\psi}{\partial y}\sin\phi\cos\theta + \frac{\partial\psi}{\partial z}\sin\theta,$$

and therefore from (2), we find

$$\begin{aligned} h_1\frac{\partial\psi}{\partial\mu} &= -\left(\frac{\partial u}{\partial t} - 2\omega v\right)\cos\phi\cos\theta - \left(\frac{\partial v}{\partial t} + 2\omega u\right)\sin\phi\cos\theta + \frac{\partial w}{\partial t}\sin\theta \\ &= \frac{\partial U}{\partial t} + 2\omega V\cos\theta. \end{aligned}$$

Similarly

$$\begin{aligned} h_2\frac{\partial\psi}{\partial\phi} &= \frac{\partial\psi}{\partial y}\cos\phi - \frac{\partial\psi}{\partial x}\sin\phi \\ &= \left(\frac{\partial v}{\partial t} + 2\omega u\right)\cos\phi - \left(\frac{\partial u}{\partial t} - 2\omega v\right)\sin\phi \\ &= \frac{\partial V}{\partial t} + 2\omega(W\sin\theta - U\cos\theta), \end{aligned}$$

and

$$\begin{aligned} h_3\frac{\partial\psi}{\partial\nu} &= \frac{\partial\psi}{\partial x}\sin\theta\cos\phi + \frac{\partial\psi}{\partial y}\sin\theta\sin\phi + \frac{\partial\psi}{\partial z}\cos\theta \\ &= \left(\frac{\partial u}{\partial t} - 2\omega v\right)\sin\theta\cos\phi + \left(\frac{\partial v}{\partial t} + 2\omega u\right)\sin\theta\sin\phi + \frac{\partial w}{\partial t}\cos\theta \\ &= \frac{\partial W}{\partial t} - 2\omega V\sin\theta. \end{aligned}$$

Allowing for the differences in the notation, the three equations just obtained agree with those given by Professor LAMB.[*] If we suppose U, V, W, ψ, each proportional to $e^{i\lambda t}$, they may be written

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[*] 'Hydrodynamics,' p. 344.

$$\left.\begin{aligned} i\lambda \mathrm{U} + 2\omega \mathrm{V} \cos\theta &= h_1 \frac{\partial\psi}{\partial\mu}, \\ i\lambda \mathrm{V} - 2\omega\,(\mathrm{U}\cos\theta - \mathrm{W}\sin\theta) &= h_2 \frac{\partial\psi}{\partial\phi}, \\ i\lambda \mathrm{W} - 2\omega \mathrm{V}\sin\theta &= h_3 \frac{\partial\psi}{\partial\nu}. \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \quad (13).$$

The equations in the form we have just written them will hold good whatever be the depth of the ocean or the ellipticity of its surface. We now proceed to introduce approximations similar to those of the last section.

In the first place we have, as in § 2, $\overline{\mathrm{W}} = \frac{\partial\zeta}{\partial t}$, and this by (12) we see is of the order h/a compared with $\overline{\mathrm{U}}$ or $\overline{\mathrm{V}}$. Hence, omitting terms of the order h/a, and of order ϵ, compared with those retained, the equations (13) take at the surface the approximate forms

$$\left.\begin{aligned} i\lambda\overline{\mathrm{U}} + 2\omega\overline{\mathrm{V}}\cos\theta &= \frac{\sqrt{(1-\mu^2)}}{a}\frac{\partial\overline{\psi}}{\partial\mu}, \\ i\lambda\overline{\mathrm{V}} - 2\omega\overline{\mathrm{U}}\cos\theta &= \frac{1}{a\sqrt{(1-\mu^2)}}\frac{\partial\overline{\psi}}{\partial\phi}, \\ -\,2\omega\overline{\mathrm{V}}\sin\theta &= \frac{\partial\psi}{\partial n'}, \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \quad (14)$$

where, in conformity with the notation of § 2, we have denoted by $\partial\psi/\partial n'$ the rate of variation of ψ in the direction of the normal to the surface of the ocean.

From the equations (14) it appears that $\partial\psi/\partial n'$ is a quantity of the same order of magnitude as $\overline{\psi}/a$; also if we apply the operator $h_3\frac{\partial}{\partial\nu}$ to each of the equations (13), we shall obtain equations which enable us to express $\partial\mathrm{U}/\partial n'$, $\partial\mathrm{V}/\partial n'$, $\partial\mathrm{W}/\partial n'$ in terms of $\overline{\mathrm{U}}$, $\overline{\mathrm{V}}$, $\overline{\mathrm{W}}$, and the surface-values of ψ and its differential coefficients. A little consideration will show that in general $\partial\mathrm{U}/\partial n'$, $\partial\mathrm{V}/\partial n'$, $\partial\mathrm{W}/\partial n'$ must be of the order $\overline{\mathrm{U}}/a$, $\overline{\mathrm{V}}/a$.

Now the approximations introduced in the last section will hold good provided that we may neglect

$$(\gamma_0 - \gamma_1)\left[\frac{\partial}{\partial\gamma}\,(\mathrm{U}/h_2h_3)\right] \text{ and } (\gamma_0 - \gamma_1)\left[\frac{\partial}{\partial\gamma}\,(\mathrm{V}/h_3h_1)\right]$$

in comparison with $[\mathrm{U}/h_2h_3]$, $[\mathrm{V}/h_3h_1]$; or, in our present notation, that we may neglect

$$h\frac{\partial}{\partial n'}\left\{c^2\sqrt{(\nu^2+\mu^2)}\,\sqrt{(1-\mu^2)}\,\mathrm{U}\right\} \text{ and } h\frac{\partial}{\partial n'}\left\{\frac{c^2(\nu^2+\mu^2)\,\mathrm{V}}{\sqrt{(1-\mu^2)}\sqrt{(1+\nu^2)}}\right\}$$

in comparison with

$$\overline{\mathrm{U}}c^2\sqrt{}(\nu_0{}^2+\mu^2)\sqrt{}(1-\mu^2),\quad \overline{\mathrm{V}}\,\frac{c^2(\nu_0{}^2+\mu^2)}{\sqrt{}(1-\mu^2)\sqrt{}(1+\nu_0{}^2)}.$$

But we have seen that $\partial\mathrm{U}/\partial n'$, $\partial\mathrm{V}/\partial n'$ are of the order $\overline{\mathrm{U}}/a$, while

$$\frac{\partial}{\partial n'}\{c^2\sqrt{}(\nu^2+\mu^2\},\quad \frac{\partial}{\partial n'}\left\{\frac{c^2(\nu^2+\mu^2)}{\sqrt{}(1+\nu^2)}\right\}$$

are of the order $c^2\nu_0/a$.

Hence

$$h\frac{\partial}{\partial n'}\{c^2\sqrt{}(\nu^2+\mu^2)\sqrt{}(1-\mu^2)\,\mathrm{U}\},\qquad h\frac{\partial}{\partial n'}\left\{\frac{c^2(\nu^2+\mu^2)\,\mathrm{V}}{\sqrt{}(1-\mu^2)\sqrt{}(1+\nu^2)}\right\}$$

are both of the order

$$\overline{\mathrm{U}}\,\frac{h}{a}\,c^2\nu_0.$$

The approximations will therefore be admissible, provided h/a is a small quantity, that is, provided that the depth of the ocean is small in comparison with the radius of the solid earth, a hypothesis as to the validity of which there can be no doubt.

Returning now to equations (14), and solving for $\overline{\mathrm{U}}$, $\overline{\mathrm{V}}$ we find

$$\overline{\mathrm{U}}(\lambda^2-4\omega^2\cos^2\theta)=-i\lambda\,\frac{\sqrt{}(1-\mu^2)}{a}\,\frac{\partial\overline{\psi}}{\partial\mu}+\frac{2\omega\cos\theta}{a\sqrt{}(1-\mu^2)}\,\frac{\partial\overline{\psi}}{\partial\phi},$$

$$\overline{\mathrm{V}}(\lambda^2-4\omega^2\cos^2\theta)=-2\omega\cos\theta\,\frac{\sqrt{}(1-\mu^2)}{a}\,\frac{\partial\overline{\psi}}{\partial\mu}-\frac{i\lambda}{a\sqrt{}(1-\mu^2)}\,\frac{\partial\overline{\psi}}{\partial\phi}.$$

But we have rigorously

$$\cos\theta=\mu\,\frac{\sqrt{}(\nu_0{}^2+1)}{\sqrt{}(\nu_0{}^2+\mu^2)},$$

and therefore, with errors of the order of the ellipticity, we may replace $\cos\theta$ by μ. Hence, finally, we obtain the values of $\overline{\mathrm{U}}$, $\overline{\mathrm{V}}$ with errors of the order h/a, ϵ compared with their true values in the form

$$\left.\begin{aligned}\overline{\mathrm{U}}&=-\frac{i\lambda\sqrt{}(1-\mu^2)}{a(\lambda^2-4\omega^2\mu^2)}\,\frac{\partial\overline{\psi}}{\partial\mu}+\frac{2\omega\mu}{a\sqrt{}(1-\mu^2)(\lambda^2-4\omega^2\mu^2}\,\frac{\partial\overline{\psi}}{\partial\phi},\\ \overline{\mathrm{V}}&=-\frac{2\omega\mu\sqrt{}(1-\mu^2)}{a(\lambda^2-4\omega^2\mu^2)}\,\frac{\partial\overline{\psi}}{\partial\mu}-\frac{i\lambda}{a\sqrt{}(1-\mu^2)(\lambda^2-4\omega^2\mu^2)}\,\frac{\partial\overline{\psi}}{\partial\phi}.\end{aligned}\right\}\quad .\;\;.\quad (15).$$

Substituting these values in the right-hand member of (12), we obtain

$$i\lambda a^2\zeta = \frac{\partial}{\partial\mu}\left\{\frac{i\lambda h(1-\mu^2)}{\lambda^2-4\omega^2\mu^2}\frac{\partial\psi}{\partial\mu} - \frac{2\omega\mu h}{\lambda^2-4\omega^2\mu^2}\frac{\partial\psi}{\partial\phi}\right\}$$

$$+\frac{\partial}{\partial\phi}\left\{\frac{2\omega\mu h}{\lambda^2-4\omega^2\mu^2}\frac{\partial\psi}{\partial\mu} + \frac{i\lambda h}{(1-\mu^2)(\lambda^2-4\omega^2\mu^2)}\frac{\partial\psi}{\partial\phi}\right\} \quad . \quad . \quad . \quad (16).$$

Hence, provided that λ be not equal to zero, we have

$$a^2\zeta = \frac{\partial}{\partial\mu}\left\{\frac{h(1-\mu^2)}{\lambda^2-4\omega^2\mu^2}\frac{\partial\psi}{\partial\mu} - \frac{2\omega\mu h}{i\lambda(\lambda^2-4\omega^2\mu^2)}\frac{\partial\psi}{\partial\phi}\right\}$$

$$+\frac{\partial}{\partial\phi}\left\{\frac{2\omega\mu h}{i\lambda(\lambda^2-4\omega^2\mu^2)}\frac{\partial\psi}{\partial\mu} + \frac{h}{(1-\mu^2)(\lambda^2-4\omega^2\mu^2)}\frac{\partial\psi}{\partial\phi}\right\} \quad . \quad . \quad (17).$$

This equation, in conjunction with the pressure equation (9) of § 2, serves to determine ψ, ζ in terms of μ, ϕ. It is equivalent to the well-known equation used by LAPLACE in the 'Mécanique Céleste.'* Omitting from consideration for the present the types of motion defined by $\lambda = 0$, we propose in the present paper to discuss only those solutions which are symmetrical with respect to the axis of rotation. In order that such solutions may exist, we must suppose that h, ψ are independent of ϕ; the equation (17) will then reduce to

$$\frac{\partial}{\partial\mu}\left\{\frac{h(1-\mu^2)}{f^2-\mu^2}\frac{\partial\psi}{\partial\mu}\right\} = 4a^2\omega^2\zeta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18),$$

where for brevity we have put $\lambda/2\omega = f$.

§ 5. *Integration by Means of Zonal Harmonics.*

Suppose that ζ is expressible as a series of zonal harmonics of the form

$$\zeta = \sum_{n=1}^{n=\infty} C_n P_n(\mu).$$

Neglecting the ellipticity of the surface, we may at once write down the value at the surface of the potential due to this distribution; we have, namely,

$$\overline{v}' = \sum_{n=1}^{n=\infty}\frac{4\pi\rho a}{2n+1} C_n P_n(\mu),$$

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* Part I., Book IV., § 3.

where the density ρ is expressed in gravitational units. But if σ denote the mean density of the earth as a whole, including the ocean, we have, with the same degree of approximation,

$$g = \tfrac{4}{3}\pi\sigma a,$$

and therefore

$$\bar{v}' = \sum_{n=1}^{n=\infty} \frac{3\rho}{(2n+1)\sigma} g C_n P_n(\mu).$$

As this only involves the ratio ρ/σ, it is independent of the unit of mass employed.

Next suppose that the surface-value of the disturbing potential can be expressed by means of the series

$$\Sigma \gamma_n P_n(\mu).$$

Then equation (9) of § 2 gives

$$\begin{aligned}\bar{\psi} &= \bar{v}' - g\zeta + \bar{v} \\ &= -\Sigma\left[g\left(1 - \frac{3\rho}{(2n+1)\sigma}\right)C_n - \gamma_n\right]P_n(\mu),\end{aligned}$$

or, if we write for brevity,

$$\left.\begin{aligned} g_n &= g\left(1 - \frac{3\rho}{(2n+1)\sigma}\right), \\ \Gamma_n &= \gamma_n - g_n C_n \end{aligned}\right\} \quad \ldots \ldots \ldots \quad (19),$$

we have

$$\bar{\psi} = \Sigma \Gamma_n P_n(\mu) \quad \ldots \ldots \ldots \quad (20).$$

Now, from the equation

$$\frac{d}{d\mu}\left\{(1-\mu^2)\frac{dP_n}{d\mu}\right\} + n(n+1)P_n = 0$$

which defines the zonal harmonics, we find

$$(1-\mu^2)\frac{dP_n}{d\mu} = -n(n+1)\int^\mu P_n\, d\mu.$$

Hence, if we integrate (18) with respect to μ, we obtain

$$\begin{aligned}\frac{h(1-\mu^2)}{f^2-\mu^2}\frac{\partial\bar{\psi}}{\partial\mu} &= 4a^2\omega^2\Sigma C_n\int^\mu P_n\, d\mu \\ &= A - 4a^2\omega^2(1-\mu^2)\Sigma\frac{C_n}{n(n+1)}\frac{dP_n}{d\mu},\end{aligned}$$

where A is an arbitrary constant, which may be seen to be zero by putting $\mu = \pm 1$. Therefore

$$h\,(1-\mu^2)\frac{\partial\bar{\psi}}{\partial\mu} = -\,4a^2\omega^2\,(1-\mu^2)\,\Sigma\,\frac{C_n}{n\,(n+1)}\,(f^2-\mu^2)\,\frac{dP_n}{d\mu} \quad . \quad . \quad (21).$$

But, by well known properties of the zonal harmonics, we have

$$\begin{aligned}(1-\mu^2)\frac{dP_n}{d\mu} &= -\,n\,(n+1)\int^{\mu} P_n\,d\mu \\ &= -\,\frac{n\,(n+1)}{2n+1}\int^{\mu}\left(\frac{dP_{n+1}}{d\mu}-\frac{dP_{n-1}}{d\mu}\right)d\mu \\ &= -\,\frac{n\,(n+1)}{2n+1}\,(P_{n+1}-P_{n-1})\end{aligned}$$

no arbitrary constant being necessary since both sides vanish when $\mu = 1$; and therefore

$$\begin{aligned}(f^2-\mu^2)\frac{dP_n}{d\mu} &= (f^2-1)\frac{dP_n}{d\mu} - \frac{n\,(n+1)}{2n+1}\,(P_{n+1}-P_{n-1}) \\ &= (f^2-1)\frac{dP_n}{d\mu} - \frac{n\,(n+1)}{2n+1}\left\{\frac{1}{2n+3}\left(\frac{dP_{n+2}}{d\mu}-\frac{dP_n}{d\mu}\right) - \frac{1}{2n-1}\left(\frac{dP_n}{d\mu}-\frac{dP_{n-2}}{d\mu}\right)\right\},\end{aligned}$$

whence

$$\begin{aligned}(f^2-\mu^2)\frac{dP_n}{d\mu} = &-\frac{n\,(n+1)}{(2n+1)(2n+3)}\frac{dP_{n+2}}{d\mu} \\ &+\left(f^2-1+\frac{2n\,(n+1)}{(2n-1)(2n+3)}\right)\frac{dP_n}{d\mu} - \frac{n\,(n+1)}{(2n-1)(2n+1)}\frac{dP_{n-2}}{d\mu}.\end{aligned}$$

This relation will hold good when $n = 1$, provided we replace $dP_{-1}/d\mu$ by zero.

Thus the right-hand member of (21) is equal to

$$4a^2\omega^2(1-\mu^2)\sum_{=1}^{n=\infty}\left[\frac{C_{n-2}}{(2n-3)(2n-1)} - C_n\left(\frac{f^2-1}{n\,(n+1)}+\frac{2}{(2n-1)(2n+3)}\right)+\frac{C_{n+2}}{(2n+3)(2n+5)}\right]\frac{dP_n}{d\mu}.$$

The left-hand member may in virtue of (20) be written in the form

$$h\,(1-\mu^2)\,\Sigma\Gamma_n\,\frac{dP}{d\mu}.$$

Equating the two members and dividing by $4\omega^2a^2\,(1-\mu^2)$, we obtain

$$\begin{aligned}&\frac{h}{4\omega^2a^2}\,\Sigma\Gamma_n\,\frac{dP_n}{d\mu} \\ &= \Sigma\,\frac{dP_n}{d\mu}\left\{\frac{C_{n-2}}{(2n-3)(2n-1)} - C_n\left(\frac{f^2-1}{n\,(n+1)}+\frac{2}{(2n-1)(2n+3)}\right)+\frac{C_{n+2}}{(2n+3)(2n+5)}\right\}.\end{aligned}$$

Hence, provided h be constant, the two members will be identical, if for all positive integral values of n we have

$$\frac{C_{n-2}}{(2n-3)(2n-1)} - C_n\left(\frac{f^2-1}{n(n+1)} + \frac{2}{(2n-1)(2n-3)}\right) + \frac{C_{n+2}}{(2n+3)(2n+5)} = \frac{h\Gamma_n}{4\omega^2a^2} \quad (22),$$

it being understood that $C_0 = 0$, $C_{-1} = 0$.

This is on the hypothesis that the depth is constant; a more general hypothesis would be to suppose that h is of the form

$$k + l(1-\mu^2)$$

where k and l are constants

Assuming this form for h, the left-hand member of (21) becomes

$$k(1-\mu^2)\Sigma\Gamma_n\frac{dP_n}{d\mu} + l(1-\mu^2)\Sigma\Gamma_n(1-\mu^2)\frac{dP_n}{d\mu},$$

which, by the properties proved above, is equal to

$$k(1-\mu^2)\Sigma\Gamma_n\frac{dP_n}{d\mu}$$

$$-\,l(1-\mu^2)\,\Sigma\left[\frac{(n-2)(n-1)}{(2n-3)(2n-1)}\Gamma_{n-2} - \frac{2n(n+1)}{(2n-1)(2n+3)}\Gamma_n + \frac{(n+2)(n+3)}{(2n+3)(2n+5)}\Gamma_{n+2}\right]\frac{dP_n}{d\mu}.$$

Identifying this with the right-hand member, we obtain

$$\frac{C_{n-2}}{(2n-3)(2n-1)} - C_n\left(\frac{f^2-1}{n(n+1)} + \frac{2}{(2n-1)(2n+3)}\right) + \frac{C_{n+2}}{(2n+3)(2n+5)}$$

$$= \frac{k\Gamma_n}{4\omega^2a^2} - \frac{l}{4\omega^2a^2}\left\{\frac{(n-2)(n-1)}{(2n-3)(2n-1)}\Gamma_{n-2} - \frac{2n(n+1)}{(2n-1)(2n+3)}\Gamma_n + \frac{(n+2)(n+3)}{(2n+3)(2n+5)}\Gamma_{n+2}\right\} \text{(22A)}.$$

On introducing the values of Γ_n from (19), equations (22), (22A) may be written

$$\frac{C_{n-2}}{(2n-3)(2n-1)} - C_n\left(\frac{f^2-1}{n(n+1)} + \frac{2}{(2n-1)(2n+3)} - \frac{hg_n}{4\omega^2a^2}\right)$$

$$+ \frac{C_{n+2}}{(2n+3)(2n+5)} = \frac{h\gamma_n}{4\omega^2a^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23),$$

$$C_{n-2}\left\{\frac{1-(n-1)(n-2)\,lg_{n-2}/4\omega^2a^2}{(2n-3)(2n-1)}\right\}$$

$$-\,C_n\left\{\frac{(f^2-1)}{n(n+1)} + \frac{2\{1-n(n+1)\,lg_n/4\omega^2a^2\}}{(2n-1)(2n+3)} - \frac{kg_n}{4\omega^2a^2}\right\}$$

$$+\,C_{n+2}\left\{\frac{1-(n+2)(n+3)\,lg_{n+2}/4\omega^2a^2}{(2n+3)(2n+5)}\right\}$$

$$= \frac{k\gamma_n}{4\omega^2a^2} - \frac{l}{4\omega^2a^2}\left\{\frac{(n-2)(n-1)}{(2n-3)(2n-1)}\gamma_{n-2} - \frac{2n(n+1)}{(2n-1)(2n+3)}\gamma_n + \frac{(n+2)(n+3)}{(2n+3)(2n+5)}\gamma_{n+2}\right\}. \text{(23A)}$$

The law of variable depth which we have assumed appears to be the most general law which will lead to a difference-relation connecting the successive C's of order not higher than the second. We shall confine ourselves chiefly to the case where the depth is uniform, but the following remark with respect to the more general case seems worthy of attention.

If we put for brevity

$$\xi_n = \frac{1 - n(n+1)\,lg_n/4\omega^2a^2}{(2n+1)(2n+3)}, \quad \eta_{n-2} = \frac{1 - n(n+1)\,lg_n/4\omega^2a^2}{(2n-1)(2n+1)},$$

$$\mathrm{L}_n = \frac{f^2-1}{n(n+1)} + \frac{2\{1 - n(n+1)\,lg_n/4\omega^2a^2\}}{(2n-1)(2n+3)} - \frac{kg_n}{4\omega^2a^2},$$

and suppose all the γ's zero, so that there is no disturbing force, equations (23A) may be written

$$\left.\begin{array}{ll} -\mathrm{L}_1\mathrm{C}_1 + \eta_1\mathrm{C}_3 = 0, & -\mathrm{L}_2\mathrm{C}_2 + \eta_2\mathrm{C}_4 = 0, \\ \xi_1\mathrm{C}_1 - \mathrm{L}_3\mathrm{C}_3 + \eta_3\mathrm{C}_5 = 0, & \xi_2\mathrm{C}_2 - \mathrm{L}_4\mathrm{C}_4 + \eta_4\mathrm{C}_6 = 0, \\ \xi_3\mathrm{C}_3 - \mathrm{L}_5\mathrm{C}_5 + \eta_5\mathrm{C}_7 = 0, & \xi_4\mathrm{C}_4 - \mathrm{L}_6\mathrm{C}_6 + \eta_6\mathrm{C}_8 = 0, \\ \cdots\cdots & \cdots\cdots \end{array}\right\} \quad . \quad . \quad . \quad (24).$$

Now, suppose l in the expression $k + l(1 - \mu^2)$ for the depth is of the form $\frac{4\omega^2a^2}{r(r+1)g_r}$, where r is an integer, and for greater definiteness let us suppose that r is even.

Then $\xi_r = 0$ and $\eta_{r-2} = 0$, and therefore the equations (24) will all be satisfied if

$$\begin{array}{rl} -\mathrm{L}_2\mathrm{C}_2 + \eta_2\mathrm{C}_4 &= 0, \\ \xi_2\mathrm{C}_2 - \mathrm{L}_4\mathrm{C}_4 + \eta_4\mathrm{C}_6 &= 0, \\ \cdots\cdots & \\ \xi_{r-4}\mathrm{C}_{r-4} - \mathrm{L}_{r-2}\mathrm{C}_{r-2} &= 0, \\ \xi_{r-2}\mathrm{C}_{r-2} - \mathrm{L}_r\mathrm{C}_r + \eta_r\mathrm{C}_{r+2} &= 0, \\ -\mathrm{L}_{r+2}\mathrm{C}_{r+2} + \eta_{r+2}\mathrm{C}_{r+4} &= 0, \\ \xi_{r+2}\mathrm{C}_{r+2} - \mathrm{L}_{r+4}\mathrm{C}_{r+4} + \eta_{r+4}\mathrm{C}_{r+6} &= 0, \\ \cdots\cdots & \end{array}$$

and all the C's with odd suffixes vanish.

Further, these will be satisfied if C_{r+2}, C_{r+4}, . . . are all zero, provided λ is a root of the equation

$$\begin{vmatrix} -L_2, & \eta_2, & 0, & 0, & \cdots & & \\ \xi_2, & -L_4, & \eta_4, & 0, & \cdots & & \\ 0, & \xi_4, & -L_6, & \eta_6 & \cdots & & \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & & & & -L_{r-6}, & \eta_{r-6}, & 0 \\ \cdots & & & & \xi_{r-6}, & -L_{r-4}, & \eta_{r-4} \\ \cdots & & & & 0, & \xi_{r-4}, & -L_{r-2} \end{vmatrix} = 0.$$

It follows that there exist certain types of free oscillation for which all the values of C with suffixes greater than r are zero. For these types the height of the surface-waves will be expressible by a finite series of terms terminating with a term involving P_r.

In like manner, if the disturbing force be derivable from a potential function of the form of a second order harmonic, the equations which determine the forced oscillations are

$$-L_2C_2 + \eta_2C_4 = \frac{k\gamma_2}{4\omega^2a^2} + \frac{4}{7}\frac{l\gamma_2}{4\omega^2a^2},$$

$$\xi_2C_2 - L_4C_4 + \eta_4C_6 = -\frac{2 \cdot 3}{5 \cdot 7}\frac{l\gamma_2}{4\omega^2a^2},$$

$$\xi_4C_4 - L_6C_6 + \eta_6C_8 = 0,$$

$$\cdots\cdots$$

$$\xi_{r-4}C_{r-4} - L_{r-2}C_{r-2} = 0,$$

$$\xi_{\cdot-2}C_{r-2} - L_rC_r + \eta_rC_{r+2} = 0,$$

$$-L_{r+2}C_{r+2} + \eta_{r+2}C_{r+4} = 0.$$

$$\cdots\cdots$$

If we suppose C_{r+2}, C_{r+4}, . . . all zero, the first $r/2$ of these equations will serve to determine C_2, C_4, . . . C_r in terms of γ_2, while the remaining equations will be satisfied identically. Thus the forced tides for the law of depth in question will be expressible by a finite series of terms terminating with a term involving P_r.

This general law does not hold when $r = 2$, owing to the presence of a term in the right-hand member of the second equation.

The fact that for these laws of depth the tide-heights could be expressed by finite series, instead of by the infinite series usually required, was originally proved by LAPLACE in the 'Mécanique Céleste.'[*]

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[*] Part I., Book IV., § 5.

§ 6. *The Period-Equation for the Free Oscillations.*

Returning to the case of uniform depth, we see that the equations (23) divide themselves into two groups, in one of which only even suffixes and in the other of which only odd suffixes are involved. We therefore conclude that the types of oscillation divide themselves into two classes, in the former of which the height of the surface-waves will be expressible entirely by harmonics of even order, and in the latter by harmonics of odd order alone. An exactly similar treatment is applicable to each of these classes; we shall therefore select for discussion the former set, contenting ourselves as regards the latter with merely stating results.

Denote by L_n the expression

$$\frac{f^2-1}{n(n+1)}+\frac{2}{(2n-1)(2n+3)}-\frac{hg_n}{4\omega^2a^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (25).$$

Then, putting all the γ's equal to zero, the types of free oscillation will be determined by the equations

$$\left.\begin{aligned}
&-C_2L_2+\frac{C_4}{7.9}=0\\
&\frac{C_2}{5.7}-C_4L_4+\frac{C_6}{11.13}=0\\
&\quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \\
&\frac{C_{n-2}}{(2n-3)(2n-1)}-C_nL_n+\frac{C_{n+2}}{(2n+3)(2n+5)}=0\\
&\quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad .
\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (26).$$

At first sight it might appear that whatever be the value of λ these equations will serve to determine $C_4, C_6, \ldots$ in succession in terms of C_2, whereas we know that this should only be possible for certain determinate values of λ corresponding to the different periods of free oscillation. The manner in which these values of λ are to be determined involves arguments similar to those used by KELVIN[*] in justification of the procedure of LAPLACE with reference to the forced oscillations after it had been attacked by AIRY[†] and FERREL[‡].

From equations (26), we obtain by actual solution

$$-\frac{C_4}{7.9}=-C_2L_2$$

$$\frac{C_6}{7.9.11.13}=C_2\begin{vmatrix}-L_2, & \dfrac{1}{7.9}\\[2mm] \dfrac{1}{5.7}, & -L_4\end{vmatrix}$$

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[*] 'Phil. Mag.', 1875. *Cf.* also an analogous problem treated by NIVEN, 'Phil. Trans.,' 1880, Part I., p. 133 *et seq.*

[†] "Tides and Waves," § 3.

[‡] "Tidal Researches" (U. S. Coast Survey 1873).

and in general

$$(-1)^{n/2}\frac{C_{n+2}}{7.9.11\ldots(2n+5)} = C_2 \begin{vmatrix} -L_2, & \frac{1}{7.9}, & 0, & 0 & \cdots & \\ \frac{1}{5.7}, & -L_4, & \frac{1}{11.13}, & 0 & \cdots & \\ 0, & \frac{1}{9.11}, & -L_6, & \frac{1}{15.17} & \cdots & \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0, & 0, & \cdots & \cdots & -L_{n-2}, & \frac{1}{(2n-1)(2n+1)} \\ 0, & 0, & \cdots & 0, & \frac{1}{(2n-3)(2n-1)}, & -L_n \end{vmatrix}$$

or, denoting the determinant which multiplies C_2 in the last equation written down by Δ_n,

$$C_{n+2} = (-1)^{n/2}\, 7.9.11 \quad . \quad . \quad . \quad (2n+5)\,\Delta_n C_2, \quad (n = 2, 4, 6, \quad . \quad . \quad . \quad)$$

Now the determinant Δ_n is an algebraic polynomial of degree $n/2$ in f^2. If therefore we equate it to zero, we should obtain an algebraic equation of degree $n/2$. If f^2 has as its value any of the $n/2$ roots of this equation the first $n/2$ of equations (26) will be consistent, while C_{n+2} will vanish. By increasing the value of n we shall approximate more and more closely to the case where an infinite number of such equations are satisfied, while we shall impose an additional condition on the C's, viz. :—that at some stage one of them must vanish. Though in general in the actual motion none of the quantities C_2, C_4, . . . are zero, they are however subject to an important restriction, namely, that the series C_2, C_4 . . . must form a converging series, and therefore we must satisfy the equation

$$\underset{n=\infty}{\mathrm{L}^t} C_{n+2} = 0.$$

The latter equation may be regarded as the period-equation for the free oscillations. It follows that as n is increased the roots of the equation $\Delta_n = 0$, which make $C_{n+2} = 0$, must approach closer and closer to certain definite limiting values, which correspond to the different periods of free oscillation, and that the series C_2, C_4 . . . calculated in succession from equations (26) can only form a convergent series when f has one of these values.

Now we see that $\Delta_n = 0$ is the equation obtained by eliminating the C's from the set of equations

$$\left.\begin{array}{ll} -C_2L_2+\frac{C_4}{7.9}=0, & \\ \cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot & \\ \frac{C_{r-2}}{(2r-3)(2r-1)}-C_rL_r+\frac{C_{r+2}}{(2r+3)(2r+5)} & =0, \\ \cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot & \\ \frac{C_{n-2}}{(2n-3)(2n-1)}-C_nL_n & =0 \end{array}\right\}\quad .\ .\ .\ .\ .\quad (27).$$

From these we obtain

$$\frac{C_{r-2}/C_r}{(2r-3)(2r-1)}=L_r-\frac{\frac{1}{(2r+3)(2r+5)}}{C_r/C_{r+2}},$$

$$=L_r-\frac{\frac{1}{(2r+1)(2r+3)^2(2r+5)}}{\frac{C_r/C_{r+2}}{(2r+1)(2r+3)}},$$

and therefore by successive applications

$$C_{r-2}/C_r=(2r-3)(2r-1)\left[L_r-\frac{\frac{1}{(2r+1)(2r+3)^2(2r+5)}}{L_{r+2}}-\ldots-\frac{\frac{1}{(2n-3)(2n-1)^2(2n+1)}}{L_n}\right].$$

Thus the eliminant of equations (27) can be expressed in the form

$$L_2=\frac{\frac{1}{7.9}}{C_2/C_4}=\frac{\frac{1}{5.7^2.9}}{L_4}-\frac{\frac{1}{9.11^2.13}}{L_6}-\ldots-\frac{\frac{1}{(2n-3)(2n-1)^2(2n+1)}}{L_n}.$$

We therefore see that the roots of the equation $\Delta_n=0$ are the roots of

$$L_2-\frac{\frac{1}{5.7^2.9}}{L_4}-\frac{\frac{1}{9.11^2.13}}{L_6}-\ldots-\frac{\frac{1}{(2n-3)(2n-1)^2(2n+1)}}{L_n}=0.$$

This form for the equation $\Delta_n=0$ has an advantage over the determinantal form, in that it enables us at once to proceed to the limit when n is made infinitely great, and thus to express the period-equation for the free oscillations by means of the transcendental equation

$$L_2-\frac{\frac{1}{5.7^2.9}}{L_4}-\frac{\frac{1}{9.11^2.13}}{L_6}-\ldots\ ad\ inf.=0\quad .\ .\ .\ .\ .\ .\quad (28).$$

We may however obtain a number of alternative forms for our period-equation. From (27) we find

$$\frac{C_{r+2}/C_r}{(2r+3)(2r+5)} = L_r - \frac{\dfrac{1}{(2r-3)(2r-1)^2(2r+1)}}{\dfrac{C_r/C_{r-2}}{(2r-1)(2r+1)}},$$

and therefore by successive applications

$$\frac{C_{r+2}/C_r}{(2r+3)(2r+5)} = L_r - \frac{\dfrac{1}{(2r-3)(2r-1)^2(2r+1)}}{L_{r-2}} \; - \dots - \; \frac{\dfrac{1}{5.7^2.9}}{L_2}$$

Thus, we have

$$L_r = \frac{\dfrac{1}{(2r-3)(2r-1)^2(2r+1)}}{\dfrac{C_r/C_{r-2}}{(2r-1)(2r+1)}} + \frac{\dfrac{1}{(2r+1)(2r+3)^2(2r+5)}}{\dfrac{C_r/C_{r+2}}{(2r+1)(2r+3)}}$$

$$= \frac{\dfrac{1}{(2r-3)(2r-1)^2(2r+1)}}{L_{r-4}} \; - \; \frac{\dfrac{1}{(2r-7)(2r-5)^2(2r-3)}}{L_{r-4}} \; - \dots - \; \frac{\dfrac{1}{5.7^2.9}}{L_2}$$

$$+ \frac{\dfrac{1}{(2r+1)(2r+3)^2(2r+5)}}{L_{r+2}} \; - \; \frac{\dfrac{1}{(2r+5)(2r+7)^2(2r+9)}}{L_{r+4}} \; - \dots - \; \frac{\dfrac{1}{(2n-3)(2n-7)^2(2n+1)}}{L_n}.$$

This is an alternative form for the equation $\Delta_n = 0$; by making n infinite, we obtain as an alternative form of the period-equation

$$L_r - \frac{\dfrac{1}{(2r-3)(2r-1)^2(2r+1)}}{L_{r-2}} \; - \; \frac{\dfrac{1}{(2r-7)(2r-5)^2(2r-3)}}{L_{r-4}} \; - \dots - \; \frac{\dfrac{1}{5.7^2.9}}{L_2}$$

$$- \frac{\dfrac{1}{(2r+1)(2r+3)^2(2r+5)}}{L_{r+2}} \; - \; \frac{\dfrac{1}{(2r+5)(2r+7)^2(2r+9)}}{L_{r+4}} \; - \dots \textit{ ad inf.} = 0 \quad (29),$$

where r is any even integer.

§ 7. *Numerical Solution of the Period-Equation.*

The method I have used to solve the above equation will perhaps be best explained by giving a numerical example in detail.

Taking for the ratio of the mean density of the earth to that of water the value given by Boys,* we deduce

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* 'Roy. Soc. Proc.,' vol. 56, 1894, p. 132.

$$\rho/\sigma = \cdot 18093,$$

whence

$$\begin{array}{ll} g_2/g = \cdot 89144 & g_{12}/g = \cdot 97829 \\ g_4/g = \cdot 93969 & g_{14}/g = \cdot 98128 \\ g_6/g = \cdot 95825 & g_{16}/g = \cdot 98355 \\ g_8/g = \cdot 96807 & g_{18}/g = \cdot 98533 \\ g_{10}/g = \cdot 97415 & g_{20}/g = \cdot 98676 \end{array}$$

the values of g_n/g approximating closer and closer to unity as n increases.

Next take $hg/4\omega^2a^2 = \frac{1}{40}$, which corresponds to a depth of $\frac{1}{2890}$ of the earth's radius, or about 7260 feet. With this value of the depth we find

$$\begin{array}{ll}
L_2 = \frac{1}{2\,.\,3}\left(\frac{\lambda^2}{4\omega^2} - 1\right) + \cdot 07295, & L_{12} = \frac{1}{12\,.\,13}\left(\frac{\lambda^2}{4\omega^2} - 1\right) - \cdot 021237, \\
L_4 = \frac{1}{4\,.\,5}\left(\frac{\lambda^2}{4\omega^2} - 1\right) + \cdot 002482, & L_{14} = \frac{1}{14\,.\,15}\left(\frac{\lambda^2}{4\omega^2} - 1\right) - \cdot 022143, \\
L_6 = \frac{1}{6\,.\,7}\left(\frac{\lambda^2}{4\omega^2} - 1\right) - \cdot 011835, & L_{16} = \frac{1}{16\,.\,17}\left(\frac{\lambda^2}{4\omega^2} - 1\right) - \cdot 022746, \\
L_8 = \frac{1}{8\,.\,9}\left(\frac{\lambda^2}{4\omega^2} - 1\right) - \cdot 017184, & L_{18} = \frac{1}{18\,.\,19}\left(\frac{\lambda^2}{4\omega^2} - 1\right) - \cdot 023168, \\
L_{10} = \frac{1}{10\,.\,11}\left(\frac{\lambda^2}{4\omega^2} - 1\right) - \cdot 019777, & L_{20} = \frac{1}{20\,.\,21}\left(\frac{\lambda^2}{4\omega^2} - 1\right) - \cdot 023476.
\end{array}$$

Introduce for brevity the notation

$$H_n = \frac{\frac{1}{(2n+1)(2n+3)^2(2n+5)}}{L_n} - \frac{\frac{1}{(2n-3)(2n-1)^2(2n+1)}}{L_{n-2}} - \ldots - \frac{\frac{1}{5\,.\,7^2\,.\,9}}{L_2},$$

$$K_n = \frac{\frac{1}{(2n-3)(2n-1)^2(2n+1)}}{L_n} - \frac{\frac{1}{(2n+1)(2n+3)^2(2n+5)}}{L_{n+2}} - \ldots - \textit{ad inf.}$$

The period-equation (29) may then be written

$$L_n - H_{n-2} - K_{n+2} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30).$$

Suppose now that $\lambda^2/4\omega^2$ has a value found by equating to zero one of the quantities L_n, say for example L_8; putting $L_8 = 0$, we obtain with the numerical values given above

$$\frac{\lambda^2}{4\omega^2} = 2\cdot 23726,$$

and with this value for $\lambda^2/4\omega^2$ we find

$$L_2 = \cdot 27916, \qquad L_{10} = -\cdot 008529,$$
$$L_4 = \cdot 064345, \qquad L_{12} = -\cdot 013306,$$
$$L_6 = \cdot 017624, \qquad L_{14} = -\cdot 016251.$$

The value of $\log \dfrac{1}{(2n+1)(2n+3)^2(2n+5)}$ is

for $n = 2$, $\bar{4}\cdot 6566$, for $n = 8$, $\bar{6}\cdot 8898$,

,, $n = 4$, $\bar{5}\cdot 8490$, ,, $n = 10$, $\bar{6}\cdot 5564$,

,, $n = 6$, $\bar{5}\cdot 3034$, ,, $n = 12$, $\bar{6}\cdot 2769$.

With these values we find for the successive convergents to the continued fraction H_6

$$\cdot 001141, \quad \cdot 001217, \quad \cdot 001219,$$

while the successive convergents to the continued fraction K_{10} are

$$-\cdot 000910, \quad -\cdot 000939, \quad -\cdot 000940, \ldots$$

It will be observed that these continued fractions converge with great rapidity; so long as the depth of the ocean is not less than that we are here using, I find that when $\lambda^2/4\omega^2$ has a value in the neighbourhood of a root of the equation $L_n = 0$, the continued fractions H_{n-2}, K_{n+2} are represented without sensible error by their fourth convergents, while in many cases the second convergents will form a sufficiently accurate approximation to their values; this rapid convergence of course greatly facilitates the numerical computation. In practice, the simplest method of evaluating the continued fractions is to assume that, for a sufficiently large value of n, $K_n = 0$, and then to compute K_{n-2}, K_{n-4}, &c., in succession from the formula

$$K_{n-2} = \frac{\dfrac{1}{(2n-7)(2n-5)^2(2n-3)}}{L_{n-2} - K_n}.$$

Thus, in the present instance, we may put $K_{16} = 0$, and deduce

$$\log K_{14} = n\bar{4}\cdot 06, \quad \log K_{12} = n\bar{4}\cdot 436, \quad \log K_{10} = n\bar{4}\cdot 9730,$$

whence, as above,

$$K_{10} = -\cdot 000940.$$

In like manner, in order to evaluate H_{n-2}, we assume that, for some sufficiently small value of r, $H_r = 0$, and then compute H_{r+2}, H_{r+4}, . . . , H_{n-2} in turn by means of the formula

$$H_{r+2} = \frac{\overline{\dfrac{1}{(2r+5)(2r+7)^2(2r+9)}}}{L_{r+2} - H_r}.$$

In the present case we find

$$\log H_2 = \bar{3}\cdot2107, \quad \log H_4 = \bar{3}\cdot0516, \quad \log H_6 = \bar{3}\cdot0860,$$

whence

$$H_6 = \cdot001219,$$

and

$$\begin{aligned} L_8 - H_6 - K_{10} &= -\cdot001219 + \cdot000940 \\ &= -\cdot000279. \end{aligned}$$

This being a small quantity we conclude that there is a root of the period-equation differing but slightly from the value assumed for $\lambda^2/4\omega^2$, namely, 2·23726. A closer approximation will be found by using this value in H_6, K_{10}, and again equating $L_8 - H_6 - K_{10}$ to zero; in other words, by putting

$$L_8 = +\cdot000279.$$

The second approximation to the root is therefore given by

$$\lambda^2/4\omega^2 = 2\cdot25735.$$

Taking this value, and proceeding as before, we find

$$\begin{aligned} L_8 - H_6 - K_{10} &= \cdot000279 - \cdot001183 + \cdot000961 \\ &= \cdot000057. \end{aligned}$$

We have now found that, when $\lambda^2/4\omega^2 = 2\cdot23726$,

$$L_8 - H_6 - K_{10} = -\cdot000279,$$

and when $\lambda^2/4\omega^2 = 2\cdot25735$,

$$L_8 - H_6 - K_{10} = +\cdot000057,$$

whence, by interpolation, we conclude that

$$L_8 - H_6 - K_{10} = 0,$$

when

$$\lambda^2/4\omega^2 = 2\cdot25394.$$

In general we shall at this stage obtain a sufficiently close approximation to the root sought, as may be verified by actual substitution. Should however great accuracy be desired, we may re-start the computation, using the value already found as a first approximation, and so continue until the desired degree of accuracy is attained. The number of cases in which I have found a repetition of the process necessary is however extremely limited.

By the method here sketched I have calculated the first six roots of the period-equation for four different depths of the ocean corresponding to the values $\frac{1}{40}$, $\frac{1}{20}$, $\frac{1}{10}$, $\frac{1}{5}$, respectively, for $hg/4\omega^2a^2$. These depths are equivalent to about 7260, 14520, 29040, 58080 feet respectively, and the results are embodied in the following tables :—

TABLE I.

	Approximate value of $\lambda^2/4\omega^2$, computed from equation $L_n = 0$.	Corrected value of $\lambda^2/4\omega^2$.	Period of oscillation expressed in sidereal time.		Corresponding period when there is no rotation.	
			h.	m.	h.	m.
Depth 7,260 feet ($hg/4\omega^2a^2 = \frac{1}{40}$); $\rho/\sigma =$ ·18093.						
$n = 2$	·56230	·44155	18	3·5	32	49
$n = 4$	·95036	·96357	12	13·5	17	30
$n = 6$	1·4971	1·5224	9	43·5	11	58
$n = 8$	2·2373	2·2539	7	59·6	9	5
$n = 10$	3·1755	3·1867	6	43·3	7	20
$n = 12$	4·3130	4·3209	5	46·4	6	9
Depth 14,520 feet ($hg/4\omega^2a^2 = \frac{1}{20}$); $\rho/\sigma =$ ·18093.						
$n = 2$	·69600	·62473	15	11·0	23	12
$n = 4$	1·4202	1·4368	10	0·7	12	23
$n = 6$	2·5032	2·5168	7	33·8	8	28
$n = 8$	3·9798	3·9882	6	0·5	6	26
$n = 10$	5·8544	5·8600	4	57·4	5	11
$n = 12$	8·1283	8·1322	4	12·5	4	21
Depth 29,040 feet ($hg/4\omega^2a^2 = \frac{1}{10}$); $\rho/\sigma =$ ·18093.						
$n = 2$	·96344	·92506	12	28·6	16	25
$n = 4$	2·3599	2·3707	7	47·6	8	45
$n = 6$	4·5155	4·5224	5	38·6	5	59
$n = 8$	7·4649	7·4691	4	23·5	4	33
$n = 10$	11·2123	11·2150	3	35·0	3	40
$n = 12$	15·7588	15·7609	3	1·4	3	4
Depth 58,080 feet ($hg/4\omega^2a^2 = \frac{1}{5}$); $\rho/\sigma =$ ·18093.						
$n = 2$	1·4983	1·4785	9	52·1	11	35
$n = 4$	4·2393	4·2453	5	49·4	6	11
$n = 6$	8·5402	8·5437	4	6·3	4	14
$n = 8$	14·4352	14·4371	3	9·5	3	13
$n = 10$	21·9275	21·9293	2	33·8	2	36
$n = 12$	31·0202	31·0212	2	9·3	2	10

By a comparison of the 2nd and 3rd columns it will be noticed that in most cases the roots of the frequency-equation are given at once with a fair degree of accuracy by simply solving the equations $L_n = 0$, and that this approximation improves the greater n becomes. In the fifth column I have given the periods of oscillation for an ocean of the same depth when the rotation is annulled, calculated by means of the formula

$$\frac{\lambda^2}{4\omega^2} = \frac{n(n+1)hg_n}{4\omega^2 a^2},$$

where ω now denotes a constant such that $\pi/\omega = 12$ hours. It will be seen that the approximation obtained by omitting the rotation continually improves with increasing values of n, but in no case will it lead to as accurate a result as the formula

$$\frac{\lambda^2}{4\omega^2} - 1 = n(n+1)\left\{\frac{hg_n}{4\omega^2 a^2} - \frac{2}{(2n-1)(2n+3)}\right\}.$$

For instance, taking the case $hg/4\omega^2 a^2 = \frac{1}{40}$, $n = 8$, the error introduced by using the first formula amounts to about 14 per cent., whereas the second form gives the frequency with an error less than one per cent. of its true value.

§ 8. *Unsymmetrical Types.*

An exactly similar method of treatment is applicable to the types which are represented by a series of harmonics of odd order; the period-equation for these types is given by

$$L_n - H_{n-2} - K_{n+2} = 0$$

where n now denotes an odd integer and H_n, K_n denote respectively the continued fractions

$$\frac{\dfrac{1}{(2n+1)(2n+3)^2(2n+5)}}{L_n} - \frac{\dfrac{1}{(2n-3)(2n-1)^2(2n+1)}}{L_{n-2}} - \dots - \frac{\dfrac{1}{3\,.\,5^2\,.\,7}}{L_1},$$

$$\frac{\dfrac{1}{(2n-3)(2n-1)^2(2n+1)}}{L_n} - \frac{\dfrac{1}{(2n+1)(2n+3)^2(2n+5)}}{L_{n+2}} - \dots \textit{ ad inf.}$$

Treating this case in the same manner as the last, I have found the first six roots and the corresponding periods of oscillation for the four depths employed as follows :—

TABLE II.

	Approximate value of $\lambda^2/4\omega^2$.	Corrected value of $\lambda^2/4\omega^2$.	Period of oscillation.		Corresponding period without rotation.	
			h.	m.	h.	m.
Depth, 7,260 feet $(hg/4\omega^2a^2 = \frac{1}{40})$; $\rho/\sigma =$ ·18093.						
$n = 1$	·24095	·15491	30	29·3	59	17
$n = 3$	·74340	·70890	14	15·2	22	49
$n = 5$	1·2002	1·2270	10	50·0	14	13
$n = 7$	1·8426	1·8633	8	47·5	10	20
$n = 9$	2·6815	2·6951	7	18·6	8	7
$n = 11$	3·7193	3·7287	6	12·9	6	41
Depth, 14,520 feet $(hg/4\omega^2a^2 = \frac{1}{20})$; $\rho/\sigma =$ ·18093.						
$n = 1$	·28191	·22204	25	28·0	41	55
$n = 3$	1·0201	1·0160	11	54·3	16	8
$n = 5$	1·9132	1·9300	8	38·3	10	3
$n = 7$	3·1919	3·2025	6	42·3	7	18
$n = 9$	4·8672	4·8741	5	26·1	5	44
$n = 11$	6·9414	6·9461	4	33·2	4	44
Depth, 29,040 feet $(hg/4\omega^2a^2 = \frac{1}{10})$; $\rho/\sigma =$ ·18093.						
$n = 1$	·36381	·32658	20	59·9	29	39
$n = 3$	1·57362	1·57822	9	33·1	11	25
$n = 5$	3·3391	3·34816	6	33·5	7	7
$n = 7$	5·8906	5·8959	4	56·5	5	10
$n = 9$	9·2387	9·2421	3	56·8	4	4
$n = 11$	13·3856	13·3880	3	16·8	3	21
Depth, 58,080 feet $(hg/4\omega^2a^2 = \frac{1}{5})$; $\rho/\sigma =$ ·18093.						
$n = 1$	·52763	·50650	16	51·7	20	58
$n = 3$	2·6806	2·6853	7	19·4	8	4
$n = 5$	6·1911	6·1957	4	49·3	5	1
$n = 7$	11·2879	11·2906	3	34·3	3	39
$n = 9$	17·9816	17·9833	2	49·8	2	52
$n = 11$	26·2742	26·2753	2	20·5	2	22

§ 9. *Numerical Computation of the Height of the Surface-Waves.*

We have next to evaluate the quantities C_2, C_4 . . . ; when once the periods have been determined this will present no difficulty. Suppose we are dealing with the type whose frequency approximates to the root of the equation $L_n = 0$; we have seen in the preceding sections how to evaluate K_{n+2}, K_{n+4}, . . . and H_{n-2}, H_{n-4}, . . . Also we have

$$C_{r+2}/C_r = (2r+3)(2r+5)K_{r+2},$$

$$C_{r-2}/C_r = (2r-3)(2r-1)H_{r-2},$$

and therefore

$$\begin{aligned} C_{n+2} &= (2n+3)(2n+5)K_n C_n, \\ C_{n+4} &= (2n+3)(2n+5)(2n+7)(2n+9)K_{n+2}K_{n+4}C_n, \\ &\quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \\ C_{n-2} &= (2n-1)(2n-3)H_{n-2}C_n, \\ C_{n-4} &= (2n-1)(2n-3)(2n-5)(2n-7)H_{n-2}H_{n-4}C_n. \\ &\quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \end{aligned}$$

Thus the height of the surface-waves is given by

$$\zeta = C_n e^{i\lambda t}\left[\begin{aligned} &\ldots + (2n-1)(2n-3)(2n-5)(2n-7)H_{n-2}H_{n-4}P_{n-4} \\ &+ (2n-1)(2n-3)H_{n-2}P_{n-2} + P_n + (2n+3)(2n+5)K_{n+2}P_{n+2} \\ &+ (2n+3)(2n+5)(2n+7)(2n+9)K_{n+2}K_{n+4}P_{n+4} + \ldots \end{aligned}\right]$$

where λ is the root of the frequency-equation in question, and C_n is an arbitrary constant.

Continuing with the particular numerical example dealt with in § 7, we take

$$\frac{\lambda^2}{4\omega^2} = 2\cdot 25394, \quad \text{or} \quad \frac{\lambda}{2\omega} = 1\cdot 5014$$

and deduce

$$\begin{aligned} L_2 &= \cdot 281944, & L_{12} &= -\cdot 013199, \\ L_4 &= \cdot 065179, & L_{14} &= -\cdot 016171, \\ L_6 &= \cdot 018021, & L_{16} &= -\cdot 01814, \\ L_8 &= \cdot 000232, & L_{18} &= -\cdot 01951, \\ L_{10} &= -\cdot 008378. \end{aligned}$$

Neglecting K_{20}, we find

$$\log K_{18} = n\,\bar{5}\cdot 535, \qquad \log K_{16} = n\,\bar{5}\cdot 7785, \qquad \log K_{14} = n\,\bar{4}\cdot 0698,$$

$$\log K_{12} = n\,\bar{4}\cdot 4397, \qquad \log K_{10} = n\,\bar{4}\cdot 9812,$$

and in like manner

$$\log H_2 = \bar{3}\cdot 2064, \qquad \log H_4 = \bar{3}\cdot 0458, \qquad \log H_6 = \bar{3}\cdot 0753;$$

from these we deduce

$$\log (C_2/C_4) = \bar{2}\cdot7505, \qquad \log (C_{10}/C_8) = n\,\bar{1}\cdot5822,$$

$$\log (C_4/C_6) = \bar{1}\cdot0414, \qquad \log (C_{12}/C_{10}) = n\,\bar{1}\cdot1994,$$

$$\log (C_6/C_8) = \bar{1}\cdot3653, \qquad \log (C_{14}/C_{12}) = n\,\bar{2}\cdot9636,$$

$$\log (C_{16}/C_{14}) = n\,\bar{2}\cdot7885,$$

$$\log (C_{18}/C_{16}) = n\,\bar{2}\cdot647\,;$$

whence, finally

$$C_2/C_8 = \cdot0014, \qquad C_{10}/C_8 = -\cdot3821,$$

$$C_4/C_8 = \cdot0255, \qquad C_{12}/C_8 = +\cdot0605,$$

$$C_6/C_8 = \cdot2319, \qquad C_{14}/C_8 = -\cdot0056,$$

$$C_{16}/C_8 = +\cdot0003,$$

$$C_{18}/C_8 = -\cdot00002.$$

Combining with our solution a second, obtained by changing the sign of i wherever it occurs, we obtain a solution in the real form

$$\zeta = C_8 \cos (\lambda t + \epsilon) \left[\begin{array}{l} \cdot0014P_2 + \cdot0255P_4 + \cdot2319P_6 + P_8 \\ \qquad - \cdot3821P_{10} + \cdot0605P_{12} - \cdot0056P_{14} + \cdot0003P_{16} - \ldots \end{array} \right],$$

where C_8, ϵ are arbitrary constants.

This determines the type of oscillation for that particular mode which is in question. It will be seen that the coefficient of P_8 predominates, and that consequently the deformation of the surface will be similar in character to that which takes place when there is no rotation, in which case the height of the surface-waves is expressed by a single harmonic term. The nodal circles will however be displaced from their positions when the rotation is annulled.

§ 10. *Numerical Expressions for the Height of the Surface-Waves.*

By the method illustrated in the preceding section I have computed the series which indicate the types of oscillation for each of the forty-eight cases for which the periods are tabulated in §§ 7, 8 ; these series are given in the following tables. To obtain the height of the surface-waves, the series here given must be multiplied by a simple harmonic function of the time of arbitrary amplitude and phase, but whose period is found from the corresponding entry in the preceding tables.

TABLE III.—Heights of Surface-Waves for Symmetrical Types.

$hg/4\omega^2a^2 = \frac{1}{40}$; (7,260 feet).

$n = 2$	$P_2 - 1\cdot2678P_4 + \cdot5267P_6 - \cdot1097P_8 + \cdot0137P_{10} - \cdot0012P_{12} + \cdot0001P_{14} - \ldots$
$n = 4$	$\cdot2373P_2 + P_4 - \cdot8753P_6 + \cdot2595P_8 - \cdot0403P_{10} + \cdot0039P_{12} - \cdot0003P_{14} + \ldots$
$n = 6$	$\cdot0269P_2 + \cdot2714P_4 + P_6 - \cdot5453P_8 + \cdot1139P_{10} - \cdot0132P_{12} + \cdot0010P_{14} - \cdot0001P_{16} + \ldots$
$n = 8$	$\cdot0014P_2 + \cdot0255P_4 + \cdot2319P_6 + P_8 - \cdot3821P_{10} + \cdot0605P_{12} - \cdot0056P_{14} + \cdot0003P_{16} - \ldots$
$n = 10$	$\ldots + \cdot0012P_4 + \cdot0196P_6 + \cdot1977P_8 + P_{10} - \cdot2934P_{12} + \cdot0373P_{14} - \cdot0028P_{16} + \cdot0001P_{18} - \ldots$
$n = 12$	$\ldots + \cdot0009P_6 + \cdot0150P_8 + \cdot1715P_{10} + P_{12} - \cdot2380P_{14} + \cdot0252P_{16} - \cdot0016P_{18} + \cdot0001P_{20} - \ldots$

$hg/4\omega^2a^2 = \frac{1}{20}$; (14,520 feet).

$n = 2$	$P_2 - \cdot7484P_4 + \cdot1707P_6 - \cdot0188P_8 + \cdot0012P_{10} - \cdot0001P_{12} + \ldots$
$n = 4$	$\cdot1286P_2 + P_4 - \cdot4070P_6 + \cdot0594P_8 - \cdot0046P_{10} + \cdot0002P_{12} - \ldots$
$n = 6$	$\cdot0069P_2 + \cdot1311P_4 + P_6 - \cdot2556P_8 + \cdot0262P_{10} - \cdot0015P_{12} + \cdot0001P_{14} - \ldots$
$n = 8$	$\cdot0002P_2 + \cdot0062P_4 + \cdot1127P_6 + P_8 - \cdot1840P_{10} + \cdot0144P_{12} - \cdot0007P_{14} + \ldots$
$n = 10$	$\ldots + \cdot0002P_4 + \cdot0048P_6 + \cdot0969P_8 + P_{10} - \cdot1432P_{12} + \cdot0090P_{14} - \cdot0003P_{16} + \ldots$
$n = 12$	$\ldots + \cdot0001P_6 + \cdot0037P_8 + \cdot0845P_{10} + P_{12} - \cdot1170P_{14} + \cdot0062P_{16} - 0002P_{18} + \ldots$

$hg/4\omega^2a^2 = \frac{1}{10}$; (29,040 feet).

$n = 2$	$P_2 - \cdot4029P_4 + \cdot0477P_6 - \cdot0027P_8 + \cdot0001P_{10} - \ldots$
$n = 4$	$\cdot0677P_2 + P_4 - \cdot1989P_6 + \cdot0144P_8 - \cdot0006P_{10} + \ldots$
$n = 6$	$\cdot0017P_2 + \cdot0651P_4 + P_6 - \cdot1259P_8 + \cdot0064P_{10} - \cdot0002P_{12} + \ldots$
$n = 8$	$\ldots + \cdot0015P_4 + \cdot0560P_6 + P_8 - \cdot0912P_{10} + \cdot0036P_{12} - \cdot0001P_{14} + \ldots$
$n = 10$	$\ldots + \cdot0012P_6 + \cdot0482P_8 + P_{10} - \cdot0712P_{12} + \cdot0022P_{14} - \ldots$
$n = 12$	$\ldots + \cdot0009P_8 + \cdot0421P_{10} + P_{12} - \cdot0583P_{14} + \cdot0015P_{16} - \ldots$

$hg/4\omega^2a^2 = \frac{1}{5}$; (58,080 feet).

$n = 2$	$P_2 - \cdot2076P_4 + \cdot0125P_6 - \cdot0004P_8 + \ldots$
$n = 4$	$\cdot0347P_2 + P_4 - \cdot0989P_6 + \cdot0036P_8 - \cdot0001P_{10} + \ldots$
$n = 6$	$\cdot0004P_2 + \cdot0326P_4 + P_6 - \cdot0627P_8 + \cdot0016P_{10} - \ldots$
$n = 8$	$\ldots + \cdot0004P_4 + \cdot0280P_6 + P_8 - \cdot0455P_{10} + 0009P_{12} - \ldots$
$n = 10$	$\ldots + \cdot0003P_6 + \cdot0241P_8 + P_{10} - \cdot0355P_{12} + \cdot0006P_{14} - \ldots$
$n = 12$	$\ldots + \cdot0002P_8 + \cdot0210P_{10} + P_{12} - \cdot0291P_{14} + \cdot0004P_{16} - \ldots$

TABLE IV.—Heights of Surface-Waves for Unsymmetrical Types.

$hg/4\omega^2a^2 = \frac{1}{40}$; (7,260 feet).

$n = 1$	$P_1 - 1{\cdot}5058P_3 + {\cdot}7106P_5 - {\cdot}1673P_7 + {\cdot}0235P_9 - {\cdot}0022P_{11} + {\cdot}0001P_{13} - \ldots$
$n = 3$	${\cdot}1221P_1 + P_3 - 1{\cdot}0907P_5 + {\cdot}3875P_7 - {\cdot}0701P_9 + {\cdot}0077P_{11} - {\cdot}0006P_{13} + \ldots$
$n = 5$	${\cdot}0161P_1 + {\cdot}2772P_3 + P_5 - {\cdot}6837P_7 + {\cdot}1688P_9 - {\cdot}0226P_{11} + {\cdot}0019P_{13} - {\cdot}0001P_{15} + \ldots$
$n = 7$	${\cdot}0010P_1 + {\cdot}0280P_3 + {\cdot}2521P_5 + P_7 - {\cdot}4498P_9 + {\cdot}0811P_{11} - {\cdot}0083P_{13} + {\cdot}0006P_{15} - \ldots$
$n = 9$	$\ldots + {\cdot}0014P_3 + {\cdot}0224P_5 + {\cdot}2137P_7 + P_9 - {\cdot}3320P_{11} + {\cdot}0468P_{13} - {\cdot}0039P_{15} + {\cdot}0002P_{17} - \ldots$
$n = 11$	$\ldots + {\cdot}0010P_5 + {\cdot}0171P_7 + {\cdot}1837P_9 + P_{11} - {\cdot}2628P_{13} + {\cdot}0304P_{15} - {\cdot}0021P_{17} + {\cdot}0001P_{19} - \ldots$

$hg/4\omega^2a^2 = \frac{1}{20}$; (14,520 feet).

$n = 1$	$P_1 - 1{\cdot}0477P_3 + {\cdot}2986P_5 - {\cdot}0396P_7 + {\cdot}0030P_9 + {\cdot}0001P_{11} + \ldots$
$n = 3$	${\cdot}0778P_1 + P_3 - {\cdot}5478P_5 + {\cdot}0993P_7 - {\cdot}0091P_9 + {\cdot}0005P_{11} - \ldots$
$n = 5$	${\cdot}0048P_1 + {\cdot}1374P_3 + P_5 - {\cdot}3156P_7 + {\cdot}0381P_9 - {\cdot}0025P_{11} + {\cdot}0001P_{13} - \ldots$
$n = 7$	${\cdot}0001P_1 + {\cdot}0068P_3 + {\cdot}1218P_5 + P_7 - {\cdot}2141P_9 + {\cdot}0190P_{11} - {\cdot}0010P_{13} + \ldots$
$n = 9$	$\ldots + {\cdot}0002P_3 + {\cdot}0054P_5 + {\cdot}1043P_7 + P_9 - {\cdot}1611P_{11} + {\cdot}0113P_{13} - {\cdot}0005P_{15} + \ldots$
$n = 11$	$\ldots + {\cdot}0001P_5 + {\cdot}0042P_7 + {\cdot}0903P_9 + P_{11} - {\cdot}1288P_{13} + {\cdot}0074P_{15} - {\cdot}0003P_{17} + \ldots$

$hg/4\omega^2a^2 = \frac{1}{10}$; (29,040 feet).

$n = 1$	$P_1 - {\cdot}6516P_3 + {\cdot}1034P_5 - {\cdot}0073P_7 + {\cdot}0003P_9 - \ldots$
$n = 3$	${\cdot}0471P_1 + P_3 - {\cdot}2726P_5 + {\cdot}0248P_7 - {\cdot}0011P_9 + \ldots$
$n = 5$	${\cdot}0013P_1 + {\cdot}0689P_3 + P_5 - {\cdot}1547P_7 + {\cdot}0093P_9 - {\cdot}0003P_{11} + \ldots$
$n = 7$	$\ldots + {\cdot}0017P_3 + {\cdot}0605P_5 + P_7 - {\cdot}1059P_9 + {\cdot}0047P_{11} - {\cdot}0001P_{13} + \ldots$
$n = 9$	$\ldots + {\cdot}0014P_5 + {\cdot}0519P_7 + P_9 - {\cdot}0800P_{11} + {\cdot}0028P_{13} - {\cdot}0001P_{15} + \ldots$
$n = 11$	$\ldots + {\cdot}0010P_7 + 0450P_9 + P_{11} - {\cdot}0641P_{13} + {\cdot}0018P_{15} - \ldots$

$hg/4\omega^2a^2 = \frac{1}{5}$; (58,080 feet).

$n = 1$	$P_1 - {\cdot}3697P_3 + {\cdot}0310P_5 - {\cdot}0011P_7 + \ldots$
$n = 3$	${\cdot}0265P_1 + P_3 - {\cdot}1361P_5 + {\cdot}0063P_7 - {\cdot}0001P_9 + \ldots$
$n = 5$	${\cdot}0003P_1 + {\cdot}0346P_3 + P_5 - {\cdot}0770P_7 + {\cdot}0023P_9 - \ldots$
$n = 7$	$\ldots + {\cdot}0004P_3 + {\cdot}0302P_5 + P_7 - {\cdot}0528P_9 + {\cdot}0012P_{11} - \ldots$
$n = 9$	$\ldots + {\cdot}0003P_5 + {\cdot}0259P_7 + P_9 - {\cdot}0399P_{11} + {\cdot}0007P_{13} - \ldots$
$n = 11$	$\ldots + {\cdot}0003P_7 + {\cdot}0225P_9 + P_{11} - {\cdot}0320P_{13} + {\cdot}0005P_{15} - \ldots$

§ 11. *Forced Tides.*

Leaving now the problem of the free oscillations, let us return to the equations of § 5, when we retain the γ's. It is obvious in the first place that a disturbing force whose potential at the surface is expressible by surface-harmonics of even order alone, or of odd order alone, will give rise to a forced oscillation of like character. Further we may consider separately the effects of the different terms in the disturbing potential and superpose the results. Suppose for example that the surface-value of the disturbing potential is expressible by the single harmonic term

$$\gamma_n P_n(\mu)\, e^{i\lambda t}$$

where we will suppose n even.

The equations (23) which determine the type may be written

$$\begin{aligned}
&- C_2L_2 + C_4/7\,.\,9 = 0\\
&C_2/5\,.\,7 - C_4L_4 + C_6/11\,.\,13 = 0\\
&\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\\
&C_{n-2}/(2n-3)(2n-1) - C_nL_n + C_{n+2}/(2n+3)(2n+5) = \gamma_n h/4\omega^2a^2\\
&C_n/(2n+1)(2n+3) - C_{n+2}L_{n+2} + C_{n+4}/(2n+7)(2n+9) = 0\\
&\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot
\end{aligned}$$

with the condition that $C_\infty = 0$; whence we obtain

$$\begin{aligned}
C_{r-2}/C_r &= (2r-3)(2r-1)\,H_{r-2}\ (r < n+1)\\
C_{r+2}/C_r &= (2r+3)(2r+5)\,K_{r+2}\ (r > n-1)
\end{aligned}$$

and therefore

$$C_n\,\{H_{n-2} + K_{n+2} - L_n\} = \gamma_n h/4\omega^2a^2,$$

or

$$C_n = \frac{\gamma_n h}{4\omega^2a^2\,(H_{n-2} + K_{n+2} - L_n)}\,.$$

Thus the height of the tide is given by

$$\zeta = \frac{\gamma_n h}{4\omega^2a^2\,(H_{n-2} + K_{n+2} - L_n)}\left[\begin{aligned}&\ldots + (2n-1)(2n-3)(2n-5)(2n-7)\,H_{n-2}H_{n-4}P_{n-4}\\ &+ (2n-1)(2n-3)H_{n-2}P_{n-2} + P_n + (2n+3)(2n+5)K_{n+2}P_{n+2}\\ &+ (2n+3)(2n+5)(2n+7)(2n+9)\,K_{n+2}K_{n+4}P_{n+4} + \ldots\end{aligned}\right]$$

The expressions H, K, L all depend on λ the frequency of the disturbing force. It is obvious from the above that the tides become very large when λ approaches a root of the equation

$$L_n - H_{n-2} - K_{n+2} = 0\,;$$

and this equation, as we have already seen, is the equation which determines the periods of free oscillation.

It is usual in Tidal Theory to express the height of the forced tides in terms of the height of the corresponding "equilibrium-tides." If we denote the height of the equilibrium-tide arising from the disturbing potential in question by $\mathfrak{C}_n P_n(\mu) e^{i\lambda t}$, we see, on omitting all the terms on the left of (23) which depend on inertia, and replacing C_n by $\mathfrak{C}_n$, that

$$hg_n \mathfrak{C}_n / 4\omega^2 a^2 = \gamma_n h / 4\omega^2 a^2 ;$$

and therefore

$$\gamma_n = g_n \mathfrak{C}_n .$$

If then ζ_0 denote the height of the equilibrium-tide, we have

$$\frac{\zeta}{\zeta_0} = \frac{hg_n/4\omega^2 a^2}{(H_{n-2} + K_{n+2} - L_n) P_n} \left[\begin{array}{l} \ldots + (2n-1)(2n-3)(2n-5)(2n-7)\, H_{n-2} H_{n-4} P_{n-4} \\ + (2n-1)(2n-3)\, H_{n-2} P_{n-2} + P_n \\ + (2n+3)(2n+5)\, K_{n+2} P_{n+2} \\ + (2n+3)(2n+5)(2n+7)(2n+9)\, K_{n+2} K_{n+4} P_{n+4} \\ + \ldots \end{array} \right]$$

The most important practical application of the above theory is the case where the disturbing potential involves only a single harmonic term of the second order, and the period of the disturbance is long compared with the period of rotation. Thus taking $\lambda^2/4\omega^2 = \cdot 00133$, $hg/4\omega^2 a^2 = 1/40$, which corresponds to the case of lunar-fortnightly tides in an ocean of depth 7260 feet, we find

$$\begin{array}{ll} L_2 = -\cdot 09349, & L_8 = -\cdot 03105, \\ L_4 = -\cdot 04745, & L_{10} = -\cdot 02886, \\ L_6 = -\cdot 03561, & L_{12} = -\cdot 02764. \end{array}$$

whence, neglecting K_{14}, we obtain in succession

$$\log K_{12} = n\bar{4}\cdot 12, \qquad \log K_{10} = n\bar{4}\cdot 432, \qquad \log K_8 = n\bar{4}\cdot 8151,$$
$$\log K_6 = n\bar{3}\cdot 3055, \qquad \log K_4 = n\bar{3}\cdot 9992.$$

Thus

$$L_2 - K_4 = -\cdot 08351,$$

$$\log (C_4/C_2) = n\bar{1}\cdot 7986, \qquad \log (C_6/C_4) = n\bar{1}\cdot 4608, \qquad \log (C_8/C_6) = n\bar{1}\cdot 2216,$$
$$\log (C_{10}/C_8) = n\bar{1}\cdot 033, \qquad \log (C_{12}/C_{10}) = n\bar{2}\cdot 88,$$

$$C_2/\mathfrak{C}_2 = \frac{\frac{1}{40}\frac{g_n}{g}}{K_4 - L_2} = \cdot 2669,$$

and therefore

$$\frac{\zeta}{\zeta_0/P_2} = \cdot 2669P_2 - \cdot 1678P_4 + \cdot 0485P_6 - \cdot 0081P_8 + \cdot 0009P_{10} - \cdot 0001P_{12} + \ldots$$

In the same manner, when $hg/4\omega^2a^2 = \frac{1}{20}$,

$$\frac{\zeta}{\zeta_0/P_2} = \cdot 4079P_2 - \cdot 1671P_4 + \cdot 0285P_6 - \cdot 0027P_8 + \cdot 0002P_{10} - \ldots;$$

when $hg/4\omega^2a^2 = \frac{1}{10}$,

$$\frac{\zeta}{\zeta_0/P_2} = \cdot 5697P_2 - \cdot 1388P_4 + \cdot 0131P_6 - \cdot 0006P_8 + \ldots;$$

and when $hg/4\omega^2a^2 = \frac{1}{5}$,

$$\frac{\zeta}{\zeta_0/P_2} = \cdot 7208P_2 - \cdot 0973P_4 + \cdot 0048P_6 - \cdot 0001P_8 + \ldots$$

The lunar-fortnightly declinational tides have been evaluated by Professor DARWIN[*] for depths which correspond with the first and third cases given above, the results being expressed in series proceeding according to ascending powers of the variable μ. If we replace the various powers of μ by their values in terms of the zonal harmonics,[†] we may deduce the following series from those given by Professor DARWIN; when $hg/4\omega^2a^2 = \frac{1}{40}$, we find

$$\frac{\zeta}{\zeta_0/P_2} = \cdot 2889P_2 - \cdot 1755P_4 + \cdot 0490P_6 - \cdot 0079P_8 + \cdot 0009P_{10} - \ldots,$$

while, when $hg/4\omega^2a^2 = \frac{1}{10}$,

$$\frac{\zeta}{\zeta_0/P_2} = \cdot 5969P_2 - \cdot 1385P_4 + \cdot 0126P_6 - \cdot 0006P_8 + \ldots$$

The difference between these expansions and those we have given above, is to be explained by the fact that we have included in our analysis the effects due to the attraction of the water on itself. I have re-computed the lunar-fortnightly tides, starting with the assumption that $\rho/\sigma = 0$, and obtained practically identical results by the two methods.

We see then that the effect of the gravitational attraction of the water is to diminish the tides, as compared with the equilibrium tides, in the first case by about 8 per cent., and in the second by about 5 per cent.

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[*] 'Encyc. Brit.,' *Art.* "Tides." § 18.

[†] FERRERS: 'Spherical Harmonics,' p. 27.

§ 12. *Lunar-Fortnightly Tides in an Ocean of Variable Depth.*

A similar method of treatment may be employed when the depth follows the less restricted law, of the form $k + l(1 - \mu^2)$, made use of in § 5. The numerical computation is greatly facilitated in this case when l takes the form $\frac{4\omega^2 a^2}{r(r+1)g_r}$ where r is a small integer, since, as we have seen, the series which express the tide-heights will then rapidly terminate.

For example, taking $r = 4$ so that

$$\frac{lg}{4\omega^2 a^2} = \frac{1}{4\,.\,5 g_4/g} = \frac{1}{4\,.\,5\left\{1 - \dfrac{\rho}{3\sigma}\right\}},$$

which makes the value of l for the earth about 15,454 feet, the values of C_2, C_4 are given by the equations

$$-L_2 C_2 = \left\{\frac{k}{4\omega^2 a^2} + \frac{4}{7}\frac{l}{4\omega^2 a^2}\right\}\gamma_2 = \left\{\frac{kg_2}{4\omega^2 a^2} + \frac{4}{7}\frac{lg_2}{4\omega^2 a^2}\right\}\mathfrak{E}_2,$$

$$\xi_2 C_2 - L_4 C_4 = -\frac{2\,.\,3}{5\,.\,7}\frac{l\gamma_2}{4\omega^2 a^2} = -\frac{2\,.\,3}{5\,.\,7}\frac{lg_2}{4\omega^2 a^2}\mathfrak{E}_2,$$

whilst all the remaining C's vanish. The notation employed is that introduced at the end of § 5.

Taking $\frac{kg}{4\omega^2 a^2} = \frac{1}{5}$, $\rho/\sigma = {\cdot}18093$, we find in the case of the lunar-fortnightly tides

$$L_2 = -{\cdot}27660, \quad L_4 = -{\cdot}23787,$$
$$\log \xi_2 = \bar{2}{\cdot}3105,$$

whence we obtain at once

$$C_2 = -\left(\frac{kg}{4\omega^2 a^2} + \frac{4}{7}\frac{lg}{4\omega^2 a^2}\right)\frac{g_2}{g}\frac{\mathfrak{E}_2}{L_2} = {\cdot}7426\mathfrak{E}_2,$$

$$C_4 = \frac{2\,.\,3}{5\,.\,7}\frac{lg_2}{4\omega^2 a^2}\frac{\mathfrak{E}_2}{L_4} + \frac{\xi_2}{L_4}C_2 = -{\cdot}0980\mathfrak{E}_2.$$

Thus, if $\frac{hg}{4\omega^2 a^2} = \frac{1}{5} + \frac{1}{4\,.\,5}\frac{g}{g_4}\sin^2\theta$, where θ denotes the co-latitude, which for a system of the dimensions of the earth makes the law of depth

$$(58080 + 15454 \sin^2\theta) \text{ feet},$$

we find for the tide-height the expression

$$\zeta = \mathfrak{E}_2\left[{\cdot}7426 P_2 - {\cdot}0980 P_4\right].$$

Similarly, when

$$h = \frac{4\omega^2a^2}{g}\left(\frac{1}{10} + \frac{1}{4.5}\frac{g}{g_4}\sin^2\theta\right) = (29040 + 15454\sin^2\theta),$$

$$\zeta = \mathfrak{C}_2[\cdot 6201P_2 - \cdot 1446P_4];$$

when

$$h = \frac{4\omega^2a^2}{g}\left(\frac{1}{20} + \frac{1}{4.5}\frac{g}{g_4}\sin^2\theta\right) = (14520 + 15454\sin^2\theta),$$

$$\zeta = \mathfrak{C}_2[\cdot 5018P_2 - \cdot 1897P_4];$$

and when

$$h = \frac{4\omega^2a^2}{g}\left(\frac{1}{40} + \frac{1}{4.5}\frac{g}{g_4}\sin^2\theta\right) = (7260 + 15454\sin^2\theta),$$

$$\zeta = \mathfrak{C}_2[\cdot 4095P_2 - \cdot 2248P_4].$$

Again, if we take

$$l = \frac{4\omega^2a^2}{6.7g_6} = 7218,$$

the series for ζ will terminate with a term involving P_6, and the values of C_2, C_4, C_6 must be computed from the equations

$$-L_2C_2 + \eta_2C_4 = \left(\frac{kg}{4\omega^2a^2} + \frac{4}{7}\frac{lg}{4\omega^2a^2}\right)\frac{\gamma_2}{g} = \left(\frac{kg_2}{4\omega^2a^2} + \frac{4}{7}\frac{lg_2}{4\omega^2a^2}\right)\mathfrak{C}_2,$$

$$\xi_2C_2 - L_4C_4 = -\frac{2.3}{5.7}\frac{l\gamma_2}{4\omega^2a^2} = -\frac{2.3}{5.7}\frac{lg_2}{4\omega^2a^2}\mathfrak{C}_2,$$

$$\xi_4C_4 - L_6C_6 = 0;$$

from which we find, when $\frac{kg}{4\omega^2a^2} = \frac{1}{5}$,

$$C_2 = \cdot 7316\mathfrak{C}_2, \qquad C_4 = -\cdot 0978\mathfrak{C}_2, \qquad C_6 = \cdot 0024\mathfrak{C}_2.$$

Thus for the law of depth

$$h = \frac{4\omega^2a^2}{g}\left\{\frac{1}{5} + \frac{1}{6.7}\frac{g}{g_6}\sin^2\theta\right\} = 58080 + 7218\sin^2\theta,$$

$$\zeta = \mathfrak{C}_2[\cdot 7316P_2 - \cdot 0978P_4 + \cdot 0024P_6];$$

in like manner, when

$$h = \frac{4\omega^2a^2}{g}\left\{\frac{1}{10} + \frac{1}{6.7}\frac{g}{g_6}\sin^2\theta\right\} = 29040 + 7218\sin^2\theta,$$

$$\zeta = \mathfrak{C}_2[\cdot 5954P_2 - \cdot 1426P_4 + \cdot 0064P_6];$$

when

$$h = \frac{4\omega^2a^2}{g}\left\{\frac{1}{20} + \frac{1}{6.7}\frac{g}{g_6}\sin^2\theta\right\} = 14520 + 7218\sin^2\theta,$$

$$\zeta = \mathfrak{S}_2[\cdot 4576\mathrm{P}_2 - \cdot 1821\mathrm{P}_4 + \cdot 0137\mathrm{P}_6];$$

and when

$$h = \frac{4\omega^2a^2}{g}\left\{\frac{1}{40} + \frac{1}{6.7}\frac{g}{g_6}\sin^2\theta\right\} = 7260 + 7218\sin^2\theta,$$

$$\zeta = \mathfrak{S}_2[\cdot 3457\mathrm{P}_2 - \cdot 2075\mathrm{P}_4 + \cdot 0234\mathrm{P}_6].$$

For other values of l we must employ a method similar to that of the last section. The general formulæ for the computation of the forced tides due to a disturbing potential of the second order are

$$\left.\begin{aligned} -\mathrm{L}_2\mathrm{C}_2 + \eta_2\mathrm{C}_4 &= \frac{k\gamma_2}{4\omega^2a^2} + \frac{4}{7}\frac{l\gamma_2}{4\omega^2a^2} = \left(\frac{kg_2}{4\omega^2a^2} + \frac{4}{7}\frac{lg_2}{4\omega^2a^2}\right)\mathfrak{S}_2 \\ \xi_2\mathrm{C}_2 - \mathrm{L}_4\mathrm{C}_4 + \eta_4\mathrm{C}_6 &= -\frac{2.3}{5.7}\frac{l\gamma_2}{4\omega^2a^2} = -\frac{2.3}{5.7}\frac{lg_2}{4\omega^2a^2}\mathfrak{S}_2 \\ \xi_4\mathrm{C}_4 - \mathrm{L}_6\mathrm{C}_6 + \eta_6\mathrm{C}_8 &= 0 \\ &\ldots\ldots\ldots \end{aligned}\right\} \quad . \quad . \quad (31),$$

where

$$\xi_n = \frac{1 - n(n+1)\,lg_n/4\omega^2a^2}{(2n+1)(2n+3)}, \qquad \eta_{n-2} = \frac{1 - n(n+1)\,lg_n/4\omega^2a^2}{(2n-1)(2n+1)},$$

$$\mathrm{L}_n = \frac{f^2-1}{n(n+1)} + \frac{2\{1 - n(n+1)\,lg_n/4\omega^2a^2\}}{(2n-1)(2n+3)} - \frac{kg_n}{4\omega^2a^2}.$$

Let us introduce the notation

$$\mathrm{H}_n = \frac{\xi_n\eta_n}{\mathrm{L}_n -}\,\frac{\xi_{n-2}\eta_{n-2}}{\mathrm{L}_{n-2}} - \ldots - \frac{\xi_2\eta_2}{\mathrm{L}_2},$$

$$\mathrm{K}_n = \frac{\xi_{n-2}\eta_{n-2}}{\mathrm{L}_n} - \frac{\xi_n\eta_n}{\mathrm{L}_{n+2}} - \ldots$$

Then it may be shewn, as in the last sections, that for values of n greater than 2,

$$\mathrm{C}_{n+2}/\mathrm{C}_n = \mathrm{K}_{n+2}/\eta_n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32),$$

and therefore the first two of equations (31) may be written

$$-\mathrm{L}_2\mathrm{C}_2 + \eta_2\mathrm{C}_4 = \left\{\frac{kg_2}{4\omega^2a^2} + \frac{4}{7}\frac{lg_2}{4\omega^2a^2}\right\}\mathfrak{S}_2,$$

$$\xi_2\mathrm{C}_2 - (\mathrm{L}_4 - \mathrm{K}_6)\,\mathrm{C}_4 = -\frac{2.3}{5.7}\frac{lg_2}{4\omega^2a^2}\mathfrak{S}_2.$$

On solving these equations we obtain

$$\left.\begin{aligned} C_2 &= -\left\{\frac{kg_2}{4\omega^2a^2}+\frac{4}{7}\,\frac{lg_2}{4\omega^2a^2}\right\}\frac{\mathfrak{C}_2}{L_2-K_4}+\frac{2.3}{5.7}\,\frac{lg_2}{4\omega^2a^2}\,\frac{H_2}{\xi_2}\,\frac{\mathfrak{C}_2}{L_4-H_2-K_6} \\ C_4 &= -\left\{\frac{kg_2}{4\omega^2a^2}+\frac{4}{7}\,\frac{lg_2}{4\omega^2a^2}\right\}\frac{K_4}{\eta_2}\,\frac{\mathfrak{C}_2}{L_2-K_4}+\frac{2.3}{5.7}\,\frac{lg_2}{4\omega^2a^2}\,\frac{\mathfrak{C}_2}{L_4-H_2-K_6} \end{aligned}\right\} \quad . \quad (33),$$

after which we can deduce C_6, C_8 . . . in succession by means of (32).

For example, taking

$$\frac{kg}{4\omega^2a^2}=\frac{1}{20}, \quad \frac{lg}{4\omega^2a^2}=\frac{1}{30},$$

which makes the law of depth for the earth

$$(14520 + 9680 \sin^2\theta) \text{ feet},$$

we find for the lunar-fortnightly tide

$$L_2 = -\cdot 13276, \quad L_4 = -\cdot 08722, \quad L_6 = -\cdot 07583,$$
$$L_8 = -\cdot 07156, \quad L_{10} = -\cdot 06955, \quad L_{12} = -\cdot 0685,$$

and

$$\log \xi_2\eta_2 = \bar{4}\cdot 1437, \quad \log \xi_4\eta_4 = n\,\bar{6}\cdot 9549, \quad \log \xi_6\eta_6 = \bar{6}\cdot 9586,$$
$$\log \xi_8\eta_8 = \bar{5}\cdot 4217, \quad \log \xi_{10}\eta_{10} = \bar{5}\cdot 578,$$

whence, if we suppose $K_{14} = 0$, we obtain in succession, from the formula

$$K_n = \frac{\xi_{n-2}\,\eta_{n-2}}{L_n - K_{n+2}},$$

$$\log K_{12} = n\,\bar{4}\cdot 75, \quad \log K_{10} = n\,\bar{4}\cdot 583, \quad \log K_8 = n\,\bar{4}\cdot 1062,$$
$$\log K_6 = \bar{4}\cdot 0758, \quad \log K_4 = n\,\bar{3}\cdot 2025.$$

Also

$$\log H_2 = n\,\bar{3}\cdot 0206, \quad \log \xi_2 = \bar{2}\cdot 3707, \quad \log \eta_2 = \bar{3}\cdot 7730;$$

whence from (33) we find

$$C_2 = \cdot 4719\,\mathfrak{C}_2, \quad C_4 = -\cdot 1852\,\mathfrak{C}_2.$$

Again

$$\log (C_6/C_4) = \log (K_6/\eta_4) = n\,\bar{2}\cdot 6976,$$
$$\log (C_8/C_6) = \log (K_8/\eta_6) = \bar{2}\cdot 3910,$$
$$\log (C_{10}/C_8) = \log (K_{10}/\eta_8) = \bar{2}\cdot 774.$$

whence finally

$$C_6 = \cdot 0092, \quad C_8 = \cdot 00023, \quad C_{10} = \cdot 00001\,;$$

and the expression for the tide-height becomes

$$\zeta = \mathfrak{C}_2 \left[\cdot 4719 P_2 - \cdot 1852 P_4 + \cdot 0092 P_6 + \cdot 00023 P_8 + \cdot 00001 P_{10} + \ldots\right].$$

As a further illustration, I have computed the series for the tide-height for the case where $h = \frac{4\omega^2 a^2}{g}\left(\frac{1}{20} - \frac{1}{30}\sin^2\theta\right)$, that is, where the depth is 14,520 feet at the poles and shallows to 4840 feet at the equator. The value of ζ in this case is as follows:—

$$\zeta = \mathfrak{C}_2 \left[\cdot 3082 P_2 - \cdot 1106 P_4 + \cdot 0467 P_6 - \cdot 0158 P_8 + \cdot 0048 P_{10} \right.$$
$$\left. - \cdot 0014 P_{12} + \cdot 0004 P_{14} - \cdot 0001 P_{16} + \ldots\right].$$

When l is positive, that is, when the depth at the equator exceeds that at the poles, the series appear to converge more rapidly than when the depth is uniform, but the opposite is the case when the water is deeper at the poles than at the equator.

§ 13. *Forced Oscillations of Infinitely Long Period.**

If we suppose λ so small that we may neglect $\lambda^2/4\omega^2$, we find, on putting $\lambda^2/4\omega^2 = 0$, for the height of the forced tides the following four series in place of those given in § 11 :—

$$\frac{\zeta}{\zeta_0/P_2} = \cdot 2661 P_2 - \cdot 1671 P_4 + \cdot 0482 P_6 - \cdot 0080 P_8 + \cdot 0009 P_{10} - \cdot 0001 P_{12} + \ldots$$

$$\frac{\zeta}{\zeta_0/P_2} = \cdot 4070 P_2 - \cdot 1666 P_4 + \cdot 0284 P_6 - \cdot 0026 P_8 + \cdot 0002 P_{10} - \ldots$$

$$\frac{\zeta}{\zeta_0/P_2} = \cdot 5689 P_2 - \cdot 1385 P_4 + \cdot 0130 P_6 - \cdot 0006 P_8 + \ldots$$

$$\frac{\zeta}{\zeta_0/P_2} = \cdot 7201 P_2 - \cdot 0973 P_4 + \cdot 0048 P_6 - \cdot 0001 P_8 + \ldots$$

The lunar-fortnightly tides therefore differ only very slightly from tides whose period is infinitely long. The difference between these latter and the solar semiannual tides will be quite inappreciable, and we may take the above series as giving a good representation of the solar long-period tides, unless the effects of friction become important for such tides.

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* Several of the conclusions of the present section have been previously arrived at by Professor LAMB ('Hydrodynamics,' chapter viii.); but, on account of the important light which they throw on the later sections, I have thought it desirable to treat the questions in some detail, even at the risk o repeating what is already well known.

The fact that when the period of the disturbing force is increased without limit the free surface does not tend to approach its equilibrium form appears at first sight to be at variance with the general laws of oscillating systems. The explanation of this apparent anomaly may perhaps be made clear by considering a simple form of "gyrostatic" system which possesses only two degrees of freedom. In the absence of frictional forces, the general equations of motion of such a system may, by a proper choice of coordinates, be expressed in the form

$$\ddot{x} - \omega\dot{y} + n^2x = \text{X},$$
$$\ddot{y} + \omega\dot{x} + m^2y = \text{Y}.^*$$

Here x, y denote the generalized coordinates of the system. Of the terms on the left, the terms $\ddot{x}$, $\ddot{y}$ are due to inertia, the terms $\omega\dot{y}$, $\omega\dot{x}$ are described by THOMSON and TAIT as "motional" forces, and the terms n^2x, m^2y as "positional" forces; X, Y are the generalized components of the external disturbing force.

If now x, y, X, Y be supposed proportional to $e^{i\lambda t}$, we find from the above equations

$$-\lambda^2x - \omega i\lambda y + n^2x = \text{X},$$
$$-\lambda^2y + \omega i\lambda x + m^2y = \text{Y},$$

whence we may obtain x, y in terms of X, Y. When the period of vibration is indefinitely prolonged, λ will approach zero as a limit, and the limiting form of the solution will in general be

$$x = \text{X}/n^2, \qquad y = \text{Y}/m^2.$$

This implies that the displacements will in general tend to acquire their equilibrium-values as the period of the disturbing force is lengthened. There will, however, be an exception to this law if one or both of the positional forces n^2x, m^2y vanish.

Let us first examine the nature of the free oscillations in such cases; omitting X, Y, and supposing that $n = 0$ while m remains finite, we have for the determination of the free motions

$$\left.\begin{aligned} -\lambda^2x - \omega i\lambda y \phantom{{}+m^2y} &= 0 \\ -\lambda^2y + \omega i\lambda x + m^2y &= 0 \end{aligned}\right\}$$

or, if we denote by u, v the generalized velocity-components so that $u = \dot{x} = i\lambda x$, $v = \dot{y} = i\lambda y$,

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[*] THOMSON and TAIT, 'Natural Philosophy,' vol. 1, p. 396 (1886 edition).

$$i\lambda(u - \omega y) = 0,$$
$$-\lambda^2 y + \omega u + m^2 y = 0.$$

These equations will be satisfied if $\lambda = 0$, $u = -\dfrac{m^2 y}{\omega} =$ const. It follows that the system is capable of a small free steady motion relative to the rotating axes, defined by

$$y = \text{const}, \qquad u = -m^2 y/\omega.$$

If both n^2x, m^2y are zero, the equations for the free motions become

$$-\lambda^2 x - \omega i\lambda y = 0,$$
$$-\lambda^2 y + \omega i\lambda x = 0\ ;$$

both of which are satisfied by supposing that x, y are small arbitrary constants, and therefore $\lambda = 0$.

In the latter case the equilibrium-state defined by $x = 0$, $y = 0$ is not the only condition of relative equilibrium, but any other configuration of the system in the neighbourhood of this one will also form a configuration of relative equilibrium.

Let us now consider the nature of the limiting forms of the forced oscillations when the period is indefinitely prolonged. In the former case we must suppose that the disturbing forces are such that they do no work when the coordinate x is varied, so that $X = 0$, as otherwise the stability of the system will be destroyed; the equations of motion for the forced oscillations then become

$$i\lambda u - \omega i\lambda y = 0,$$
$$-\lambda^2 y + \omega u + m^2 y = Y\ ;$$

whence

$$u = \omega y = \frac{Y\omega}{\omega^2 + (m^2 - \lambda^2)}$$

and in the limit

$$u = \frac{Y\omega}{m^2 + \omega^2},\ y = \frac{Y}{m^2 + \omega^2}.$$

The velocity-component u will therefore always remain of the same order as the disturbing force Y, while the amplitude of vibration of the coordinate x will tend to increase without limit.

In the latter case the equations of disturbed motion may be written

$$i\lambda u - \omega v = X$$
$$i\lambda v + \omega u = Y$$

whence in the limiting case

$$u = \mathrm{Y}/\omega, \quad v = -\mathrm{X}/\omega.$$

Hence both the velocity-components tend to finite limits while the amplitudes of vibration of both coordinates increase without limit.

The essential characteristics of both cases are (i) that one or more of the generalized coordinates does not appear explicitly in the equations of motion but only the corresponding velocity-component, and hence (ii) that $\lambda = 0$ is one root of the frequency-equation for the free modes of vibration, from which it follows that (α) either free steady motions relatively to the rotating system are possible, or (β) that the configuration of relative equilibrium defined by $x = 0$, $y = 0$ is not isolated. The two conditions (α), (β) may both be expressed by stating that the steady motion defined by $x = 0$, $y = 0$ is not the only form of steady motion of which the system is capable.

The two cases are both illustrated by our problem. For if we suppose the waters of the ocean displaced horizontally in such a manner that the form of the surface is unaltered, we shall evidently obtain a new configuration of relative equilibrium, while, as we shall see in the next section, if we suppose that the fluid is in relative motion in such a manner that the fluid particles are moving along parallels of latitude, it is possible by a proper adjustment of the free surface to ensure that such a motion should be permanent.

The coordinates which depend on the horizontal displacements alone are analogous to the coordinate x in the former of the illustrations we have given above, and to the coordinates x, y in the latter. They do not appear explicitly in the equations of motion, but only through the corresponding velocity-components. We conclude, then, that the horizontal velocities will be of the order of the disturbing forces, whereas the horizontal excursions of the fluid particles will tend to increase without limit as the period is prolonged.

By way of explaining how these circumstances may arise physically, let us suppose for the moment that λ is actually zero, and consequently that the disturbing force is constant. In the case of a system oscillating about a position of equilibrium, the introduction of a constant disturbing force will have the effect of slightly changing the configuration about which oscillations corresponding with the free modes of vibration take place. Suppose now that a disturbing force, such as that which gives rise to the long-period tides, tending to increase the surface-ellipticity of the ocean, is suddenly applied to our rotating system when in a configuration of relative equilibrium. It will immediately set up oscillations, the initial motion being such that each particle will tend towards the position in which it would be in equilibrium under the new disturbing influence. The new position of equilibrium is such that in it there will be more water in equatorial regions, and less water in polar regions, than in the old. Thus the initial motion involves a flow of water directed from the poles towards the equator. The water however coming from higher latitudes into lower will reach these lower latitudes with an amount of rotation less than that which is appropriate for these latitudes if the whole were in a state of steady motion as a rigid body. There are no forces acting which tend to modify the angular momentum about the polar axis of an elementary ring of water, which coincides with a parallel of latitude, and consequently currents will be started, in virtue of which each particle of fluid will move along a parallel of latitude from east to west. The effect of the disturbing force is therefore to modify the state of steady motion about which the free oscillations take place from a uniform rotation of the whole system as a rigid body to a state in which there exist horizontal westerly currents. If, as is usual in dealing with forced oscillations, we suppose the free oscillations to be annulled, we see that the "forced oscillation" arising from such a constant disturbance as we have been considering will be of the nature of a steady motion relatively to the rotating earth, consisting of a westerly flow of the whole ocean, the velocity however varying with the latitude.

In the case of a periodic disturbance of very long period, the motion set up at any instant will be of like character, provided that the viscosity of the fluid is not sufficient to sensibly affect the currents in question in the course of a single period. An equilibrium-theory will only be applicable when the rate of dissipation of such motions is so rapid that they practically disappear in a time which is short compared with the period of the disturbing force. Now in an ocean whose depth is equal to the mean depth of the actual ocean, it seems highly improbable that such currents would be appreciably affected by viscosity in the course of a few months. Hence it appears that the present theory in which the effects of viscosity are totally disregarded will almost certainly give a far better representation of the lunar long-period tides than the equilibrium theory, and most probably also of the long-period solar tides.

§ 14. *Free Steady Motions.*

In the last section we have called attention to the fact that free oscillations of infinite period are possible, or that the system with which we are concerned is capable of free steady motions. We proceed in the present section to examine the nature of these steady motions.

Referring back to §§ 2–4, we see that the general equations of motion of the ocean when free from external disturbing influence, and at the same time supposed steady, so that $\lambda = 0$, can be expressed in the form

$$\left.\begin{aligned}
\frac{\partial\zeta}{\partial t} &= -\frac{1}{a}\left[\frac{\partial}{\partial\mu}\{\surd(1-\mu^2)\,h\,\mathrm{U}\} + \frac{\partial}{\partial\phi}\left\{\frac{h\mathrm{V}}{\surd(1-\mu^2)}\right\}\right],\\
\mathrm{U} &= -\frac{1}{2\omega a\mu\,\surd(1-\mu^2)}\frac{\partial\psi}{\partial\phi},\\
\mathrm{V} &= \frac{\surd(1-\mu^2)}{2\omega a\mu}\frac{\partial\psi}{\partial\mu},\\
\psi &= v' - g\zeta
\end{aligned}\right\} \quad . \quad . \quad (34).$$

where, as there is no longer any ambiguity, we have omitted the bars from the symbols U, V, ψ, v'.

Since $\partial\zeta/\partial t = 0$ when the motion is steady, we see that the first equation is identically satisfied if we suppose h, ψ both independent of ϕ. In this case we may take

$$\zeta = \Sigma\,\mathrm{C}_n\mathrm{P}_n(\mu) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35),$$

where the constants C_n are arbitrary, and deduce

$$\psi = -\,\Sigma\,g_n\mathrm{C}_n\mathrm{P}_n(\mu);$$

whence

$$\mathrm{V} = -\frac{\surd(1-\mu^2)}{2\omega a\mu}\,\Sigma\,g_n\mathrm{C}_n\frac{d\mathrm{P}_n}{d\mu}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36).$$

The last equation gives the velocity which must be imposed on the particles of water in latitude $\sin^{-1}\mu$ in order that the free surface may be maintained in the form defined by (35) without any external force. We see that it is theoretically possible to maintain an arbitrary surface-form by correctly distributing the longitudinal velocities of the fluid particles. If however the series (35) involves harmonics of odd order the value of V given by (36) becomes infinite at the equator, and to prevent a flow of liquid across the equator it would be necessary to impose an infinite velocity on the particles of water there. Hence, if the water extend either wholly or partially over both hemispheres, the distribution of velocity and the form of free surface must be symmetrical with respect to the equator, at least so far as concerns that part of the ocean which communicates across the equator.

Conversely, any arbitrary initial distribution of longitudinal velocity symmetrical with respect to the equator may be rendered permanent by an appropriate adjustment of the free surface. These results hold good whatsoever be the law of depth, provided it be a function of the latitude alone.

If ψ be not supposed independent of ϕ, we see from the second and third of equations (34) that the velocity of flow across any element ds inclined at an angle χ to the meridian is

$$\begin{aligned} &\mathrm{U}\sin\chi - \mathrm{V}\cos\chi, \\ &= -\frac{1}{2\omega a\mu}\left\{\sin\chi\frac{1}{\sqrt{(1-\mu^2)}}\frac{\partial\psi}{\partial\phi} + \cos\chi\sqrt{(1-\mu^2)}\frac{\partial\psi}{\partial\mu}\right\}, \\ &= -\frac{1}{2\omega\mu}\frac{\partial\psi}{\partial s}. \end{aligned}$$

Hence, if $\partial\psi/\partial s = 0$, there will be no flow across the element ds. It follows that the function ψ may be regarded as a stream-function, the paths of the particles of water always coinciding with the lines

$$\psi = \text{const.}$$

But from the equation of continuity we have, on putting $\partial\zeta/\partial t = 0$, and replacing U, V by their values in terms of ψ,

$$0 = \frac{\partial}{\partial\mu}\left\{\frac{h}{\mu}\frac{\partial\psi}{\partial\phi}\right\} - \frac{\partial}{\partial\phi}\left\{\frac{h}{\mu}\frac{\partial\psi}{\partial\mu}\right\},$$

or

$$\frac{\partial}{\partial\mu}\left(\frac{h}{\mu}\right)\frac{\partial\psi}{\partial\phi} - \frac{\partial}{\partial\phi}\left(\frac{h}{\mu}\right)\frac{\partial\psi}{\partial\mu} = 0,$$

the general solution of which is

$$\psi = f(h/\mu) \quad \text{. . . . .} \quad (37),$$

where $f(h/\mu)$ denotes an arbitrary function of h/μ.

It follows that the stream-lines $\psi =$ const coincide in direction with the lines

$$h/\mu = \text{const} \quad \text{. . . . .} \quad (38).$$

Thus, if the depth be a function of the latitude alone, the stream-lines must necessarily coincide with the parallels of latitude, and the only forms of steady motion possible are those in which the water has no latitudinal velocity. In the more general case, the stream-lines of the possible steady motions are given by the equation (38), and from this equation they might at once be traced out on a chart if we had a sufficient knowledge of the depth of the ocean in different parts. In particular, whatever be the law of depth, the equator will be one of the free stream-lines corresponding to an infinite value of h/μ, while the shores will also be stream-lines corresponding to zero values of this expression. An infinite number of stream-lines will converge towards those points where the coast-line intersects the equator, and it is only by passing through one of these points that a particle of water could pass from the northern to the southern hemisphere, or *vice versâ*. As however the velocities at these particular points tend to become infinite, the equations which we have used which involve the neglect of the squares of the velocities will not be applicable to the region immediately surrounding the points in question. It seems most probable that the inclusion of the terms involving the squares of velocities would have the effect of diverting the stream-lines, so as to cause them to follow the coast-lines even in the immediate neighbourhood of the equator.

An attempt to trace out the lines $h/\mu =$ const for the North Atlantic Ocean from data obtainable from the Admiralty charts quickly showed that the theory here put forward is inadequate in itself to explain even the more salient features of the circulation in the region in question. Observation however indicates the direction in which we must look for the defects of this theory. The excessively low temperature of the water beneath the surface[*] in equatorial regions can only be explained by supposing that this water has travelled thither from higher latitudes, whereas we know that the currents at the surface, for the most part, set from the equator towards the poles. We conclude that the under-currents of the actual ocean differ materially from the surface-currents, and in this respect the actual circulation differs from the types of circulation with which we have hitherto been concerned and which are the only possible types of circulation in our ideal ocean in which the density is uniform. It has been urged by some authorities that the variations in the density of the water arising from differences of temperature, salinity, &c., are the sole causes which maintain ocean currents, but in that we have seen that currents could exist even without such variations, it seems to me to be highly improbable that such is the case, though there can be no doubt, in the light of our present analysis, that these variations are largely effective in determining the course which the currents pursue.

If we suppose that the ocean consists of a number of horizontal layers of different densities, but that the density throughout each stratum is uniform, then for each of the strata a function ψ will exist defined by

$$\psi = V' + \tfrac{1}{2}\omega^2(x^2 + y^2) - \frac{p}{\rho} + \text{const},$$

and the horizontal velocities for any stratum will be connected with the corresponding function by the equations (34). The equation of continuity for any stratum may be formed as in § 3, provided we replace h by the depth of the stratum in question instead of the depth of the whole ocean. The stream-lines for any stratum will therefore still be given by the equation (38), with this modification in the meaning of the symbol h. It follows that the equator will still be one of the free stream-lines, but the motion elsewhere may be totally different from what it would be if the density were the same throughout. It seems probable then that the result we have obtained with reference to the tendency of the currents to set along the equator will still hold good even when the density is variable, and this conclusion is borne out by observation, it being noticeable at a glance at the Admiralty current charts that there is no tendency to cross the equator except in the immediate neighbourhood of the coasts.

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[*] The principal facts at present known in relation to the distribution of temperature in the ocean will be found in the 'Report of the *Challenger* Scientific Results,' 'Chemistry and Physics,' vol. 1.

The rigorous treatment of the problem of ocean currents, as affected by variations in the density of the water, appears to be hopelessly beyond the powers of mathematical analysis, and I will therefore leave the subject with the brief indications already given in this section, and will conclude the paper with an example illustrating another means by which possibly ocean currents are in part maintained, and which is instructive in showing the very important part played by the rotation of the earth in rendering effective a cause which otherwise could give rise to no sensible currents.

§ 15. *On Currents due to Evaporation and Precipitation.*

A cause which has been advocated* in explanation of ocean currents is the fact that in equatorial regions the amount of water evaporated into the atmosphere largely exceeds that precipitated in the form of rain in these regions. The excess of water in the atmosphere is carried away to be precipitated in temperate and polar regions, thereby giving rise to an excess of precipitation over evaporation in the latter regions. It has been urged with some reason that, as the actual amount of water in equatorial regions does not diminish nor that in polar regions increase from year to year, there must be a continual flow of water from the poles towards the equator. The fact that this flow of water is in the opposite direction to that observed at the surface, which for the most part sets from the equator towards the poles, is explained by attributing the counterflow to undercurrents. If however we subject the question to the test of mathematical analysis, we shall find that though such a flow towards the equator must necessarily exist, it is so slow as to be completely masked by larger currents due to other causes. The flow in question will however give rise indirectly, in consequence of the rotation, to currents which in the absence of dissipative forces would tend to increase without limit. The explanation of this fact will be obvious after the discussions of § 11.

The effects of evaporation and precipitation may be conveniently represented mathematically by an appropriate distribution of sources and sinks over the free surface. This will modify the surface-conditions at the free surface but will not interfere with the dynamical equations. Instead of equating $\overline{W}$ to $\partial\zeta/\partial t$ we must replace it by a certain function of the position on the surface, independent of the time, but depending on the rate of evaporation and precipitation at the place, which over sufficiently long intervals of time we may regard as uniform. A simple law which will serve for purposes of illustration may be chosen as follows:—

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* See an Article by PROCTOR in 'St. Paul's Magazine,' Sept., 1869, reprinted in 'Light Science' (1st series), p. 114.

$$\overline{W} = -\alpha P_2(\mu).$$

The equations with which we have to deal will then be

$$\left.\begin{aligned} \frac{\partial U}{\partial t} + 2\omega\mu V &= \frac{\sqrt{(1-\mu^2)}}{a}\frac{\partial\psi}{\partial\mu} \\ \frac{\partial V}{\partial t} - 2\omega\mu U &= \frac{1}{a\sqrt{(1-\mu^2)}}\frac{\partial\psi}{\partial\phi} \\ \alpha P_2(\mu) &= \frac{1}{a}\left[\frac{\partial}{\partial\mu}\{\sqrt{(1-\mu^2)}\,hU\} + \frac{\partial}{\partial\phi}\left\{\frac{hV}{\sqrt{(1-\mu^2)}}\right\}\right] \end{aligned}\right\} \quad . \quad . \quad (39),$$

where, if we neglect the attraction due to the surface-inequalities, we may take

$$\psi = -g\zeta.$$

To obtain a particular solution of these equations suppose

$$\psi = -g\zeta = -g(\zeta_0 + \zeta_1 t), \quad U = U_0 + U_1 t, \; V = V_0 + V_1 t,$$

where ζ_0, ζ_1, &c., are all independent of t.

Substituting these expressions in the equations (39), and equating coefficients of t, we find

$$\begin{aligned} 2\omega\mu V_1 &= -\frac{g}{a}\sqrt{(1-\mu^2)}\frac{\partial\zeta_1}{\partial\mu} \\ 2\omega\mu U_1 &= \frac{g}{a}\sqrt{(1-\mu^2)}\frac{\partial\zeta_1}{\partial\phi} \\ 0 &= \frac{1}{a}\left[\frac{\partial}{\partial\mu}\{\sqrt{(1-\mu^2)}\,hU_1\} + \frac{\partial}{\partial\phi}\left\{\frac{hV_1}{\sqrt{(1-\mu^2)}}\right\}\right]. \end{aligned}$$

If h be a function of μ alone, these will be satisfied by

$$U_1 = 0, \quad V_1 = -\frac{g\sqrt{(1-\mu^2)}}{2a\omega\mu}\frac{\partial\zeta_1}{\partial\mu},$$

provided ζ_1 be also a function of μ alone.

Next, if we equate the terms independent of t in the two members of (39), we obtain

$$\begin{aligned} U_1 + 2\omega\mu V_0 &= -\frac{g}{a}\sqrt{(1-\mu^2)}\frac{\partial\zeta_0}{\partial\mu} \\ V_1 - 2\omega\mu U_0 &= -\frac{g}{a}\frac{1}{\sqrt{(1-\mu^2)}}\frac{\partial\zeta_0}{\partial\phi} \\ \alpha P_2(\mu) &= \frac{1}{a}\left[\frac{\partial}{\partial\mu}\{\sqrt{(1-\mu^2)}\,hU_0\} + \frac{\partial}{\partial\phi}\left\{\frac{hV_0}{\sqrt{(1-\mu^2)}}\right\}\right]. \end{aligned}$$

Suppose the system starts from rest in its position of relative equilibrium, so that $\zeta = 0$ when $t = 0$, or $\zeta_0 = 0$. Then

$$U_1 + 2\omega\mu V_0 = 0$$
$$V_1 - 2\omega\mu U_0 = 0,$$

whence,

$$V_0 = -\frac{U_1}{2\omega\mu} = 0$$

$$U_0 = \frac{V_1}{2\omega\mu} = -\frac{g}{4\omega^2 a}\frac{\sqrt{(1-\mu^2)}}{\mu^2}\frac{\partial\zeta_1}{\partial\mu},$$

and therefore

$$\alpha P_2(\mu) = -\frac{g}{4\omega^2 a^2}\frac{\partial}{\partial\mu}\left\{\frac{(1-\mu^2)h}{\mu^2}\frac{\partial\zeta_1}{\partial\mu}\right\}.$$

The last equation gives

$$\frac{(1-\mu^2)h}{\mu^2}\frac{\partial\zeta_1}{\partial\mu} = -\frac{4\omega^2 a^2}{g}\alpha\int P_2(\mu)\,d\mu$$
$$= -\frac{4\omega^2 a^2}{g}\alpha\frac{\mu^3-\mu}{2},$$

no arbitrary constant being added, since both sides vanish when $\mu = \pm 1$. Thus,

$$h\frac{\partial\zeta_1}{\partial\mu} = \frac{2\omega^2 a^2}{g}\alpha\mu^3,$$

or

$$\zeta_1 = \frac{2\omega^2 a^2\alpha}{g}\int\frac{\mu^3}{h}\,d\mu.$$

Suppose for example that h is constant; we shall then obtain

$$\zeta_1 = \tfrac{1}{2}\frac{\omega^2 a^2\alpha}{gh}\mu^4 + \text{const}$$
$$= \tfrac{1}{2}\frac{\omega^2 a^2\alpha}{gh}\{\tfrac{8}{35}P_4 + \tfrac{4}{7}P_2 + \tfrac{1}{5}\} + \text{const}.$$

Choosing the constant so that the mean value of ζ_1 over the surface is zero, we obtain finally

$$\zeta_1 = \tfrac{1}{2}\frac{\omega^2 a^2\alpha}{gh}\{\tfrac{8}{35}P_4 + \tfrac{4}{7}P_2\}.$$

Hence the particular solutions of the differential equations which represent the "forced" motion due to the disturbing influence in question are

$$\zeta = \zeta_1 t = \frac{2\omega^2 a^2 \alpha t}{35gh}\{2\mathrm{P}_4 + 5\mathrm{P}_2\},$$

$$\mathrm{U} = \mathrm{U}_0 + \mathrm{U}_1 t = -\tfrac{1}{2}\frac{a}{h}\alpha\mu\sqrt{(1-\mu^2)},$$

$$\mathrm{V} = \mathrm{V}_0 + \mathrm{V}_1 t = -\frac{\alpha a\omega t}{h}\mu^2\sqrt{(1-\mu^2)}.$$

We see then that the effects of evaporation and precipitation will be to cause a steady flow of water, not by means of undercurrents only, but by currents sensibly uniform throughout the depth, towards the equator; in addition to these currents the cause in question will give rise to longitudinal currents, not of a steady character, but increasing uniformly with the time, and these will be accompanied by an appropriate continuous deformation of the free surface. Were it not for viscosity these currents would increase without limit and ultimately endanger the stability of the system, but under the action of dissipative forces a steady state must ultimately be attained, in which the rate at which the currents are generated exactly balances that at which they are destroyed. Thus, suppose the type of motion set up is such that if left to itself it would be reduced in the ratio $1 : e$ in a period τ. If U denote the velocity of any particle, the law of variation of U under the influence of viscous forces is then

$$\partial\mathrm{U}/\partial t + \mathrm{U}/\tau = 0,$$

whereas, if there be no viscosity and the system is subjected to such a disturbance as we have been dealing with, the velocity varies according to the law

$$\partial\mathrm{U}/\partial t = f,$$

where f is constant. Equating the rate of increase of the velocity without viscosity to the rate of decrease under the influence of dissipative force, we find that the ultimate state is defined by

$$\mathrm{U}/\tau = f, \quad \text{or} \quad \mathrm{U} = f\tau.$$

Thus, if the disturbing influence tends to set up one of the possible types of motion of which the system is capable under viscosity, the ultimate velocity of any particle will be that which it would acquire in a period equal to the modulus of decay of the type of motion in question.

By way of numerical illustration, take a year as the unit of time and an inch as the unit of length, and suppose $\alpha = 40$. This will imply an annual rainfall at the poles which exceeds evaporation by 40 inches, and an annual rainfall at the equator which is less than evaporation by 20 inches. Further, suppose $h/a = \frac{1}{2890}$. Then

$$\mathrm{U} = -\tfrac{1}{2} \times 2890 \times 40\,\mu\sqrt{(1-\mu^2)}.$$

U will be numerically greatest when $\mu^2 = \frac{1}{2}$, or in latitude 45°, and the greatest value of U is 28,900. The maximum latitudinal velocity will therefore amount to 28,900 inches, or about half-a-mile, per annum. This velocity will be quite inappreciable to observation.

The amount of longitudinal velocity generated in the course of a year in any latitude is given by the formula

$$\frac{a\alpha\omega}{h}\mu^2\sqrt{(1-\mu^2)}.$$

This will be greatest when $\mu^2 = \frac{2}{3}$, that is, in latitude 55° nearly, and its greatest value corresponds to a velocity of about $\frac{1}{5}$ of a mile per hour. The maximum current velocity due to this cause would therefore amount to about four miles per hour if the modulus of decay is as long as 20 years.

The most crucial test to which we can subject the theory of ocean currents here put forward will consist in the evaluation of the moduli of decay for the types of motion concerned. This I have endeavoured to do, but as the work involves analytical considerations of a somewhat different character from those which occur in the present work, I have deemed it advisable to present the results in a separate paper.* These results, so far as they are applicable, seem to point to a modulus of decay far in excess of the 20 years here required, but the mathematical difficulties have compelled me, in dealing with friction, to leave the rotation entirely out of account. It appears that in the simpler system so treated, the types of free current motion are far more arbitrary in character than those at which we have arrived by including the rotation. This arises from the fact that our rotating system will be capable of a large number of free oscillatory motions besides those which we have examined in which the periods of oscillation always bear a finite ratio to the period of rotation. As the period of rotation is lengthened, the period of each of these types of oscillation is prolonged, and the possible forms of steady motion where there is no rotation must include the limiting forms of each of these types of oscillatory motion.

The moduli of decay of the free current motions when there is rotation may therefore be very different in value from those obtained in the paper referred to, but it does not seem to me that they could be much less in order of magnitude than the moduli of decay of the principal types of free oscillation. If this prove to be the case, the estimate of 20 years, which we have taken for the modulus of decay, will not be so excessive as might at first sight appear.

Of course, if the water does not cover the whole earth, or if the depth be not uniform, the currents due to the rotation will follow the free stream-lines defined by equation (38) instead of following the parallels of latitude. The rotation will, no doubt, produce its maximum effect when the stream-lines in question coincide with the parallels of latitude, but this circumstance does not alter our main conclusion as to the adequacy of evaporation and other such causes to generate currents quite comparable with those known to exist in the ocean.

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* Read before the London Mathematical Society, December 10th, 1896.

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X. *Preliminary Report on the Results obtained in Novaya Zemlya with the Prismatic Camera during the Eclipse of the Sun, August 9th,* 1896.

By J. NORMAN LOCKYER, *C.B., F.R.S.*

Received November 17,—Read November 19, 1896.

[PLATE 9.]

I STATE in another communication the arrangements made for obtaining results with prismatic cameras in Lapland, and how the attempts failed through bad weather.

After the instruments had been dispatched to Lapland in H.M.S. "Volage," Sir GEORGE BADEN-POWELL, K.C.M.G., M.P., generously, and with admirable public spirit, offered to take an expedition to Novaya Zemlya in his yacht "Otaria," if observers and instruments were forthcoming. Sir GEORGE BADEN-POWELL consulted me on the subject, and ultimately, with the authority of the Vice-President of the Council, Mr. SHACKLETON, one of the computers employed by the Solar Physics Committee, was detailed to form part of the expedition.

The prismatic camera available was that which had been used in Brazil during the solar eclipse of 1893. The object glass is a DALLMEYER doublet of 19 inches equivalent focal length, with an aperture of 3·25 inches; the image of the inner corona, therefore, is a ring of 0·2 inch diameter. Two prisms of 3 inches clear aperture were used, with their refracting edges perpendicular to the horizontal, each having a refractive angle of 60°, the light being reflected into the apparatus by a siderostat. The length of the spectrum given by this combination was 1·5 inches, from F to K, or 2·3 inches, from D_3 to K.

In 1893, the photographs obtained by this instrument in Brazil were not in focus in the ultra-violet, in consequence of the difficulties of adjustment under eclipse conditions. The precaution was taken, therefore, of making all the necessary adjustments by obtaining some stellar photographs with the instrument before it left England. Ultimately, a photograph of α Lyræ left nothing to be desired, and the then positions of all the parts were carefully marked.

Three specially-constructed dark slides, carrying eight plates each ($4\frac{1}{4} \times 1\frac{5}{8}$ inches), were employed, the change from plate to plate being effected by means of a rack and pinion attached to the dark slides. The plates used were EDWARDS' isochromatic.

The following table, based on data furnished by the results of the 1893 eclipse, gives the lengths of exposures and times in totality which I drew up for use at a station on the central line in Novaya Zemlya :—

PROVISIONAL Table of Exposures.

No. of Plate.	Exposures.	Time in totality.	Remarks.
		Slide No. 1.	
1	Instantaneous	−30 seconds	Before totality
2	,,	−20 ,,	
3	,,	−15 ,,	
4	,,	−10 ,,	
5	,,	− 8 ,,	
6	3 seconds	0 ,,	Totality begins
7	10 ,,	5–15 ,,	
8	3 ,,	17–20 ,,	
		Change to Slide No. 2.	Chromosphere goes
9	2 seconds	25–27 seconds	
10	20 ,,	29–49 ,,	
11	40 ,,	51–91 ,,	
12	5 ,,	93–98 ,,	
13	Instantaneous	100 ,,	Chromosphere again visible
14	10 seconds	102–112 ,,	
15	Instantaneous	114 ,,	
16	Waste		
		Slide No. 3.	
17	Instantaneous	119 seconds	A series of snapshots, hoping to include the flash
18	,,	121 ,,	
19	,,	123 ,,	
20	,,	125 ,,	
21	,,	127 ,,	
22	,,	129 ,,	
23	,,	131 ,,	
24	,,	133 ,,	

Unfortunately, however, the expedition found it impossible to reach the central line of totality, and the duration was consequently shortened by 25 seconds. Mr. SHACKLETON, therefore, made the necessary alterations in the exposures, and the following revised table was determined upon.

Column 1 contains the numbers of the photographic plates, which will be quoted in subsequent references ; Column 2 gives the exposures ; Column 3 gives the times of exposing the plates in totality.

The exposures were made by means of a card moved by hand in front of the prisms, and when this was done as quickly as possible the exposures are tabulated as "instantaneous."

Revised Table of Exposures.

No. of Plate.	Exposures.	Time in totality.	Remarks.
		Slide No. 1.	
1	Instantaneous	−30 seconds	
2	„	−20 „	
3	„	−10 „	
4	„	0 „	Totality begins
5	3 seconds	3–6 „	
6	10 „	8–18 „	
7	3 „	20–23 „	Chromosphere goes
8	2 „	25–27 „	
		Slide No. 2.	
9	Waste	——	
10	2 seconds	35–37 seconds	
11	40 „	39–79 „	
12	5 „	81–86 „	
13	Instantaneous	88–89 „	Chromosphere reappears
14	10 seconds	91–101 „	
15	Waste		
16	„		
		Slide No. 3.	Sun reappears
17	Instantaneous	109 seconds	
18	„	110 „	A series of snapshots
19	„	113 „	
20	„	115 „	
21	Waste	..	
22	Instantaneous	117 „	
23	„	119 „	
24	„	121 „	

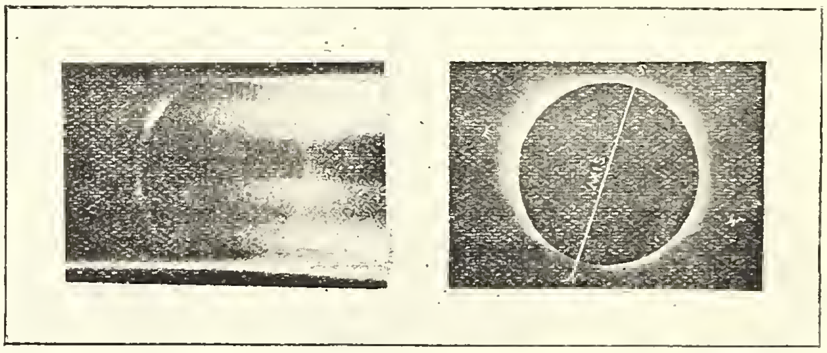
As the final reduction of the photographs will take some considerable time, I think it of importance to give at once, for the benefit of other workers, reproductions of two of the best photographs obtained. These are reproduced in Plate 9.

No. 4 is given in two sections, on a scale of 3·4 times that of the original negative. It was taken instantaneously at the exact beginning of totality. The principal arcs are those of hydrogen and the H and K lines seen in the spectrum of calcium; these long arcs, together with the numerous short ones, represent the spectrum of the sun's limb at the moment of totality, Mr. Shackleton determining the exact instant by watching the disappearance of the bright continuous spectrum with the aid of a small direct-vision slitless spectroscope. This plate may undoubtedly be said to have been exposed within 0·5 second after the commencement of totality; it had an instantaneous exposure, and this was sufficient to give a record of the spectrum from D_3 to H_μ in the ultra-violet.

No. 11 is on a scale of 2·1 times that of the original negative, being exposed for a period of 40 seconds, beginning at 39 seconds from the commencement of totality, so that it records the spectrum near mid-totality. The two overlapping disconnected rings to the left are the images of the prominences round the sun's limb represented in the H and K light, the other discontinuous rings to the right are the images in H_δ, H_γ, and H_β radiations respectively, the ring further to the right, which is of more continuous structure than the others is the 1474 K ring of the corona spectrum.

There are other fainter rings, both of the prominences and the corona, which are well seen on the original negative, but it is too much to hope that these will be seen in the Plate, being lost in the process of reproduction.

Fig 1.



1474 K ring. Corona.

Fig. 1 shows an enlargement of the 1474 K ring compared with an oriented photograph of the lower corona. It will be seen that the prismatic camera has picked out the brightest parts of the corona, and where it is strongest the spectrum ring and the continuous spectrum at those points are most intense, whilst a prominence occurring at any point of the sun's limb does not alter the intensity of the ring at the corresponding part.

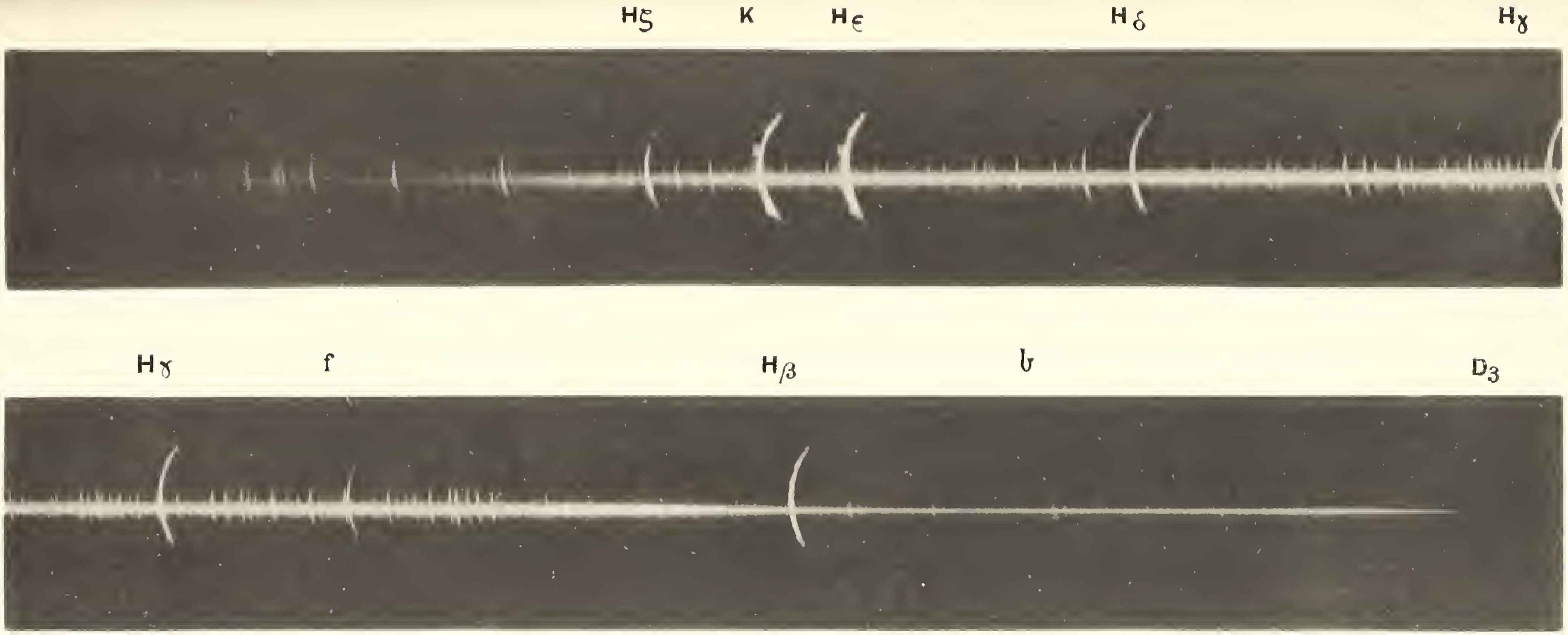
The wave-lengths of the lines in Photo No. 11 have been measured by Dr. W. J. S. LOCKYER, and a preliminary comparison of the results obtained in 1893 and 1896 has shown many points of difference; it also indicates that the photograph of the flash so happily caught by Mr. SHACKLETON, and the cusp photograph secured by Mr. FOWLER, in 1893, both represent the spectrum of the chromosphere.

Except in the case of the lines visible in the spectrum of hydrogen, and the cleveite gases and the longest lines in the spectra of some of the metallic elements, notably calcium and strontium, there is little or no relation between the intensities of the lines visible in the chromosphere and Fraunhofer spectrum.

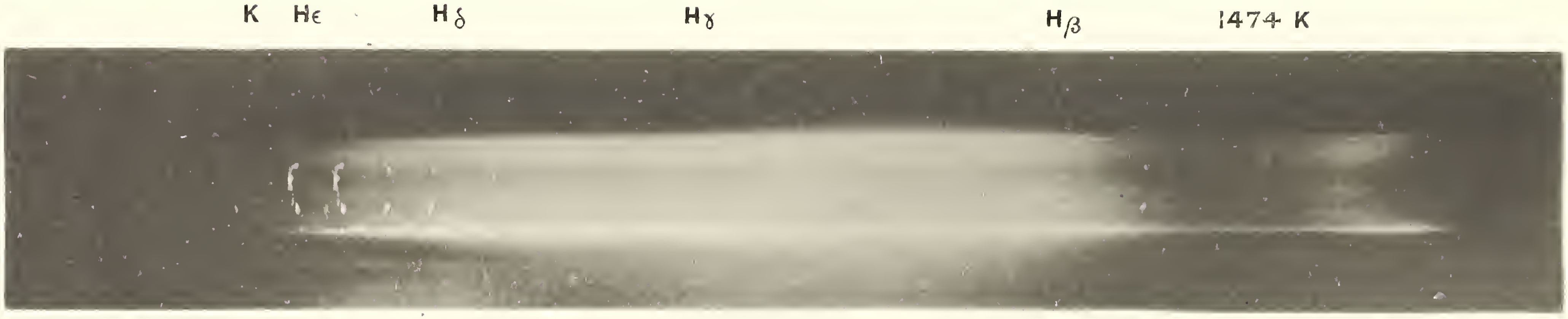
There is already evidence that the photographs which we owe to the public spirit of Sir GEORGE BADEN-POWELL and the energy and skill displayed by Mr. SHACKLETON will considerably widen our knowledge of solar physics and chemistry.

Mr. SHACKLETON's report on the local arrangements, and the complete discussion of the results of the observations in their relation to solar physics will form the subject of a subsequent communication. The investigation of the chemical origins of the various lines will occupy some time, and it seems desirable that the results of 1893 and 1896 should be studied together. These will also be communicated at some future date.

The enlarged photographs from which the accompanying plate has been prepared, and those on which the wave-lengths have been measured, have been prepared by Corporal HASLAM, R.E.



REPRODUCTION OF PHOTO. 4 IN TWO PORTIONS SHEWING ARCS



REPRODUCTION OF PHOTO. 11 SHEWING CORONAL RING IN 1474 LIGHT.

BRITISH MUSEUM
NATURAL HISTORY.

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XI. *Condensation of Water Vapour in the Presence of Dust-free Air and other Gases.*

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Communicated by Professor J. J. Thomson, *F.R.S.*

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The behaviour of air saturated with aqueous vapour and allowed to expand suddenly, has been investigated by Coulier,[*] Aitken,[†] Kiessling,[‡] and R. v. Helmholtz.[§] As is well known, if the moist air has been previously freed from "dust," no condensation takes place except on the walls of the vessel, even if the expansion be sufficient to produce considerable supersaturation. For convenience, the term "dust" is here used to include all nuclei which can be removed either by filtering or by repeatedly forming a cloud by expansion and allowing it to settle.

What is the limit, if such exists, to the degree of supersaturation which can be attained without condensation taking place throughout the moist air, is a question of considerable meteorological as well as purely physical interest. It was primarily with the object of finding an answer to this question that the experiments to be described were undertaken, such experimental evidence as already existed on the subject being of a very incomplete and contradictory character.

Aitken[||] observed condensation when a large quantity of steam was passed into a receiver containing air which had been filtered through cotton wool. Kiessling[¶] also produced a rainlike condensation in the same way. The latter observer also states that if saturated filtered air be even slightly expanded, scattered drops are formed visible only in direct sunlight. Again, Aitken[**] mentions that in his dust-counting experiments, in which sudden expansion of the saturated air was produced by means of an air-pump, a very quick stroke of the pump was found to produce a shower of drops even in filtered air, while a slow steady one had no such effect. The increase of volume was always the same, and amounted to one-third of the initial volume. He attributes the difference to the shock which results from a rapid stroke of the pump.

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[*] 'Journal de Pharmacie et de Chimie," vol. 22, pp. 165 and 254, 1875.

[†] 'Trans. Roy. Soc.,' Edin., vol. 30, p. 337, 1880–81, and vol. 35, p. 1, 1890; 'Proc. Roy. Soc.,' Lond., vol. 51, p. 408, 1892.

[‡] 'Hamburger Abhandl. der Naturwissenschaften,' vol. 8, 1884; 'Götting. Nachr.,' p. 122, 1884, and p. 226, 1884.

[§] 'Wied. Ann.,' vol. 27, p. 509, 1886.

[||] 'Trans. Roy. Soc.,' Edin., vol. 30, p. 337.

[¶] 'Götting. Nachr.,' p. 226, 1884.

[**] 'Trans. Roy. Soc.,' Edin., vol. 35, p. 1, 1890.

R. v. HELMHOLTZ,[*] on the other hand, was unable to observe any trace of condensation in saturated filtered air, even with a fall of pressure of half an atmosphere. Whether, however, the pressure was reduced from one atmosphere to one-half, or from one-and-a-half atmospheres to one, is not clear; from his description of the method one would naturally take the latter interpretation. He deduces, however, a theoretical lowering of 50° C., and a ten-fold supersaturation which correspond to the former alternative.

BARUS,[†] who made an extensive series of observations on the colour phenomena of a steam jet under varying conditions as to boiler-pressure and the temperature and dust contents of the surrounding air, concluded that with sufficient supersaturation, condensation takes place independently of dust. He does not appear, however, to have been able to deduce from his measurements the degree of supersaturation which is required to bring about this condensation.

None of the experiments referred to above are entirely free from objection.

When steam is blown into filtered air, as was done by AITKEN and KIESSLING, it is likely to carry over with it small drops of spray from the boiler. Even if these drops be made to evaporate by superheating the steam, each will leave behind a nucleus consisting of the solid matter which it contained in solution or suspension.

The condensation noticed by KIESSLING with very slight expansion may have been due to a similar cause, for he appears to have brought the air in his apparatus into a saturated state by allowing it to bubble through water after it had been filtered. That such treatment does actually introduce nuclei requiring only a slight expansion of the saturated air to cause condensation upon them is proved by certain experiments described below. AITKEN[‡] noticed, too, that if the water in his dust-counting apparatus was allowed to splash about, such nuclei were produced.

In none of the experiments mentioned above was the expansion very rapid, the apparatus in no case having been specially designed for the purpose of investigating this particular question. HELMHOLTZ's failure to obtain condensation may easily be explained by the expansion not being sufficiently rapid to produce anything like the theoretical lowering of temperature as, indeed, he himself admits.

The interpretation of steam-jet experiments, such as those of BARUS, is very difficult, especially as the phenomena depend largely on the roughness or smoothness of the bore of the nozzle from which the steam escapes. They cannot be taken as proving beyond doubt that condensation may be made to take place by increasing the supersaturation alone, as so many of the conditions besides the degree of supersaturation must vary as the initial pressure of the steam, and consequently the velocity with which it escapes from the nozzle are increased.

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[*] HELMHOLTZ, *loc. cit.*

[†] "Report on the Condensation of Atmospheric Moisture;" U.S. Department of Agriculture, Weather Bureau, 1895; also 'Phil. Mag.,' vol. 38, p. 19, 1894.

[‡] 'Edin. Trans.,' vol. 35, p. 17, 1890.

Conditions to be satisfied by the Expansion Apparatus.

To obtain unequivocal proof of the production of condensation in moist air, free from all extraneous nuclei, it is necessary that we should not be dependent upon any process of filtering, for it might always be objected that the filtering apparatus only removed those particles which exceeded a certain size.

If, however, we expand repeatedly the same sample of moist air, while protecting it from all chance of contamination, we are able to test whether all nuclei of a permanent kind have been removed. For by making an expansion rather greater than is sufficient to cause condensation, and allowing the drops formed to settle, we remove in this way a certain proportion at least, and if the drops be few and large, almost the whole of the nuclei which are able to cause condensation with this degree of supersaturation.

If this process can be repeated indefinitely without any diminution in the number of drops formed, we are justified in concluding that the nuclei are being replaced by others as fast as they are removed, and are thus an essential part of the structure of the moist gas.

It is desirable also that the expansion should admit of accurate measurement and be exceedingly rapid, so that the lowest temperature and maximum supersaturation reached may be calculated with as small an error as possible due to the influx of heat during the expansion.

In a note[*] read before the Cambridge Philosophical Society, I gave an account of some preliminary results obtained with a form of apparatus which I believed to satisfy these conditions. It was there stated that condensation results from the sudden expansion of saturated dust-free air when v_2/v_1 exceeds a value not differing much from 1·258, where v_1, v_2 are the volumes of the air before and after expansion.

No description of the apparatus was published, as it was then in quite a rudimentary condition.

The first series of experiments to be described here was carried out with an improved apparatus of the same type.

Apparatus used in the first series of Experiments.

This is represented in vertical section in fig. 1.

The air to be expanded is contained in the inverted cylindrical glass vessel A, fixed like a diving-bell below the surface of the water, which nearly fills the outer vessel B.

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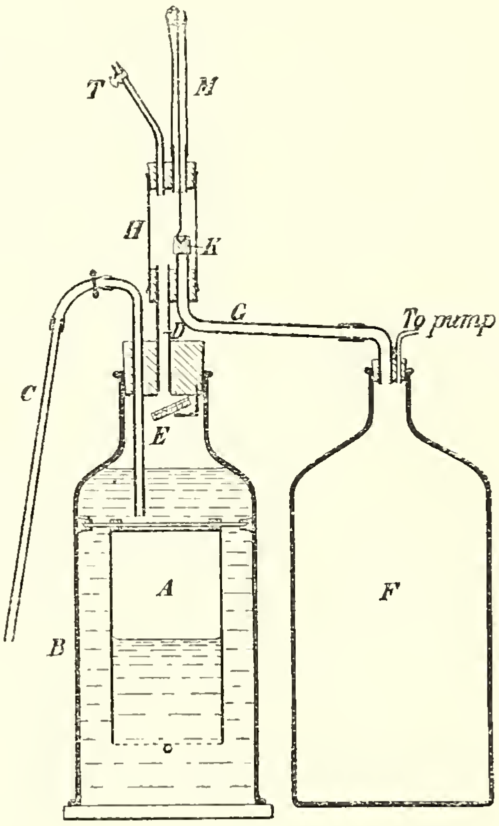
[*] 'Proc. Camb. Phil. Soc.,' vol. 8, p. 306, 1895.

The latter is a bell-jar of the form shown in the figure, resting on a ground-glass plate, to which it is wired down, and having a wide neck, closed by an indiarubber cork through which pass two glass tubes, the one, C, serving to regulate the quantity of water in B, and provided with a pinch-cock; through the other, D, the air occupying the upper part of B can be suddenly removed by opening communication with a large exhausted stoneware bottle F.

The water is prevented from following the air by means of the valve E.

Fig. 1.



The result is a sudden expansion of the air in A. The increase in volume is equal to the volume of the space in the upper part of B occupied by air before the expansion, and can therefore be made more or less by running a little water out, or drawing some more in through the tube C.

By opening the tap T, which communicates with the atmosphere, air is admitted through the tube D, and the air in A contracts to its original volume.

To bring about very sudden communication with the exhausted vessel F, the arrangement shown in the upper part of the figure was used. A short glass tube, H, is closed at both ends by indiarubber corks, each bored to receive two glass tubes. Of these, D and T have already been referred to. The tube G, which leads to the vacuum vessel F, has its upper end ground smooth, and upon this rests the flat surface of an indiarubber cork K. This closes the opening of the tube in a perfectly air-tight manner, when the air above it is at atmospheric pressure, and the pressure in F is a small fraction of this, as it always was maintained during a series of experiments.

K can be pulled up by means of the vertical wire shown in the diagram, thus rapidly making free communication between D and G and causing the expansion. The tap T must of course previously be closed. In order that one may be able to work the arrangement from the outside without admitting air, the wire passes up through a thin-walled indiarubber tube, M, closed at its upper end by a cork in which the end of the wire is fixed. A cord attached to this cork and passing over a smooth peg fixed vertically above it, enables the observer to make the expansion, while watching the behaviour of the air in the cloud chamber A.

The tubes D and G had an internal diameter of about 8 millims., so that the fall of pressure in the air-space in the upper part of B must be very rapid. The valve E, which prevented the water in the bell-jar B from following the air into the tube D, was made by cutting a thin slice from the end of an indiarubber cork and supporting it with the smooth surface uppermost on a piece of cork just thick enough to float it. It was fixed by means of a wire hinge to the lower surface of the indiarubber cork of the bell-jar, in such a position that when raised by the water reaching it, it covered the hole bored for the tube D. The latter did not quite reach the lower surface of the indiarubber cork, so that when the valve closed the contact was between two indiarubber surfaces.

This valve was found to work perfectly when the excess of pressure below was sufficient, and smooth indiarubber surfaces were used.

The bell-jar had a diameter of about 14 centims. and was about 30 centims. high. The inner vessel had a diameter of about 9 centims. A vertical glass scale, divided into millimetres, fixed by means of sealing-wax to the outside of the inner vessel, enables the observer to note with the aid of a telescope the level of the water before and after expansion. From a subsequent calibration the initial and final volumes are obtained.

To make visible any condensation in the form of fog or rain, the light from a luminous gas-flame is brought by means of a convex lens to a focus at the centre of the cloud chamber A. Any condensation which may result is most distinctly seen when the eye is placed just out of reach of the directly transmitted light. This method of illumination was used both by AITKEN and R. v. HELMHOLTZ. The experiments were performed in a dark room. When an expansion was made the only source of light was that mentioned above. After the result had been noted, light was admitted by raising a shutter in order that the readings of volume might be made.

The inside of the inner vessel, A, was cleaned before use, first with caustic potash and then with nitric acid, and well washed with distilled water. After this treatment the water forms a uniform film over the surface of the glass, instead of collecting into drops and preventing a satisfactory view of the interior.

This apparatus appeared to fulfil very well the purpose for which it was designed. Nothing can gain access to the air imprisoned in the inner vessel except by solution in and diffusion through the surrounding water.

The water surface which forms the lower boundary to the space occupied by the air under observation, drops suddenly to a new position, where it comes to a sudden stop, without any splashing, and remains stationary as long as may be desired. The whole movement is certainly over in a small fraction of a second, as the expansion appears to the eye to be instantaneous. That it should be rapid is what one would expect, as the initial driving pressure is nearly one atmosphere, and the distance travelled rarely amounted to more than two centimetres.

There is this further advantage in such a method of expanding the air, that the rate of expansion is most rapid just before it is completed, because the driving pressure still remains considerable, and the water is therefore moving with constantly increasing velocity until it brings itself to a sudden stop by closing the valve E.

Thus the final stage of the expansion, when the temperature is lowest, and therefore the influx of heat most rapid, is that which is most quickly passed through.

The motion of the water cannot, of course, be stopped instantaneously ; in practice it was always found that some small air bubbles were left imprisoned around the valve E. These, being compressed by the impact, probably served to diminish considerably the strain on the apparatus.

With a thin float the volume of these bubbles was quite a negligible fraction of that of the air which escaped before the valve closed. If any considerable fraction of the air were left behind when the valve closed, an error would be introduced by its momentary compression, the actual maximum value reached being really greater than what is afterwards measured by an amount equal to the momentary diminution in the total volume of the air bubble.

Method of Conducting the Experiments.

To charge the apparatus with air reasonably free from laboratory gases, the bell-jar, with the inner vessel fixed inside it, was removed from the ground-glass plate on which it rested, and allowed to remain at an open window for some time. It was then placed on the glass plate, and bound tightly down with wire.

Distilled water, which had been boiled for some time to remove the greater part of the dissolved gases, was then poured in till it nearly filled the bell-jar. By inclining the whole, air was allowed to escape from the inner vessel till only a convenient volume remained. The bell-jar was then again nearly filled up with water, and the apparatus then connected up as already described and shown in fig. 1.

The glass-plate was levelled by means of levelling screws supporting the tripod on which the plate was fixed. The reading telescope was then fixed some distance off, on a level with the surface of the water in the inner vessel.

Some water was now allowed to escape through the tube C, and the level of the water read on the glass scale by means of the telescope. The tap T was then closed, expansion made by pulling the cord which opens communication with the vacuum vessel F, and the effect on the contents of the expansion chamber A noted. The new level of the water in the inner vessel was again read by the telescope, and the air made to contract to its former volume by opening the tap T. The same expansion could be repeated as often as was wished, or the air could be expanded to a greater extent by first running out a little water through C. If it was desired to try the effect of a smaller expansion the tap T was only slightly opened, and was closed before the water in B had quite returned to its original level. Then the pinch-cock on the tube C was opened for a moment while the end of the tube was dipped into a beaker of water.

To find the volumes corresponding to the various readings, the bell-jar, with its inner vessel, was removed from the glass plate after every series of observations, and fixed in an inverted position so that the water could be poured into the inner vessel. The whole arrangement was then adjusted so that the ground surface of the rim of the bell-jar was level. The weight of water which had to be poured in to fill the inner vessel up to the various readings on the scale was then determined, the telescope being fixed in exactly the same relative position as in the expansion experiments.

General Account of the Phenomena Observed.

The air was generally admitted into the apparatus in the way already described, and, therefore, without any attempt to remove dust by filtering. Repeated expansion of saturated air, as AITKEN has shown, removes all "dust" particles, and this method was generally employed in these experiments.

The first expansion made, whether large or small in amount, unless the air had been allowed to stand for many hours in the apparatus, always produced a fog. This was allowed to settle as completely as possible before allowing the air to contract to its original volume. In this way a considerable proportion of the dust was removed, the particles being carried down by the drops which condensed upon them into the water below.

When this process was several times repeated, the resulting fog became by degrees coarser-grained, the drops being both fewer and larger, and therefore, falling more quickly. The fog passed at length into a fine rain. When this stage was reached one more expansion was generally sufficient to remove the remainder of the dust particles, and any further expansion, unless it exceeded the limit spoken of below, was without visible effect.

AITKEN* was able to remove all the dust particles from saturated air by repeatedly increasing its volume by $\frac{1}{50}$ of its initial amount. An even smaller expansion was found in these experiments to be sufficient for that purpose, but the time taken for the removal of the dust was naturally much shorter when larger expansions were used, on account of the larger size and more rapid fall of the drops in the latter case.

If, after the dust has been removed in this way the successive expansions be made greater and greater, no visible effect is produced till v_2/v_1, the ratio of the final to the initial volume, is equal to about 1·252. When v_2/v_1 exceeds this value a shower of drops is invariably produced. The drops are not very numerous, even with considerably greater expansions, yet, however often we expand the air, no diminution in the number of the drops can be detected.

Now, when, owing to the presence of dust particles, a shower of similar density is produced with a smaller expansion, all the dust particles appear to be carried down with the water drops, and the next expansion produces no condensation.

Thus, the nuclei which enables condensation to take place when the expansion exceeds the limit mentioned, are only present in small numbers at any given time, but as fast as they are removed they are replaced by others of the same kind.

Expansion required to produce Rain-like Condensation in Dust-free Saturated Air.

A large number of observations must generally be made in order to obtain within narrow limits a single determination of the ratio of v_2 to v_1 when condensation just takes place.

When expansions of comparatively small amount had ceased to cause condensation, each increase in volume was made considerably greater than the preceding, till a shower of drops was observed. Then an observation was made with the apparatus adjusted to give a rather smaller final volume (the initial volume remaining practically constant), and perhaps no condensation seen. By making in this way a series of alternately greater and smaller expansions of gradually diminishing difference, a stage was at length reached when the smallest measurable difference in the final volume was sufficient to determine whether condensation should result or not.

A large number of experiments were made during the summer of 1895. Only the results of the last series of measurements then made are given in the table which follows. The apparatus has been improved from time to time and the later experiments were carried out exactly as described above.

The mean of the results previously obtained for the critical value of v_2/v_1, however, is practically identical with that given below, and all the determinations of this ratio have results lying between 1·24 and 1·26.

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* 'Edin. Trans.,' 35, p. 1.

In the following table, v_1 is the initial volume and v_2 the final volume when the expansion is just sufficient to cause rain-like condensation.

	Date.	$t°$ C.	v_1	v_2	v_2/v_1
1.	September 4	22·0	292·9	367·3	1·254
2.	" 4	22·4	293·4	367·8	1·253
3.	" 5	28·8	313·1	392 5	1·253
4.	" 5	27·2	308·5	385·8	1·250
5.	" 6	27·8	312·5	390·8	1·250
6.	" 6	26·0	309·8	386·7	1·248
7.	" 7	24·5	302·0	378·3	1·252
				Mean	1·252

The same air was used on September 7 as on the previous day; otherwise the experiments were made on a different sample of air each day.

It will be noted that the expansion required is sensibly the same at all temperatures between 22° and 28° C. Accurate measurements of the initial temperature are therefore unnecessary in these experiments.

The results given in the table show no greater variation than are to be expected from the degree of accuracy of the volume measurements. The level of the water could be read by means of the telescope to the nearest tenth of a millimetre, corresponding to an error of half a cubic centimetre in the volume measurements. There may be an error of this amount in the measurement of both v_1 and v_2, and hence an error of 4 units in the fourth figure in the ratio, when the initial volume amounts to about 300 cub. centims.

Other Experiments made with the same Apparatus.

1. When sunlight was used to illuminate the drops, exactly the same expansion was required to bring about visible condensation.

The result, therefore, does not depend on the kind of illumination used.

2. Experiments were made to see if the nuclei which cause the rain-like condensation could be removed by repeated filtering. For this purpose a hole was bored through the glass plate on which the apparatus rested. A glass tube reaching to the roof of the inner vessel was passed through a cork which closed this hole. Through it the air could be drawn out into an inverted WOLFF's bottle, arranged to act as an aspirator, and could be driven from the one vessel to the other as often as was desired.

A tightly-packed cotton-wool filter was inserted between the expansion apparatus and the WOLFF's bottle. Passing the air repeatedly backwards and forwards through the filter was found to be without effect upon the appearance of the rain-like condensation, or the expansion required to produce it.

3. When no cotton-wool filter was present the air could be passed from the one vessel to the other and back without any effect, so long as it was not allowed to bubble through the distilled water in either vessel. If, however, the air had to bubble through water on being driven back, quite a small expansion was sufficient to cause a shower even some minutes later.

4. As already stated, the air may be allowed to expand considerably more than is necessary to produce condensation without the drops becoming very numerous.

With very great expansions, however, if, for example, the increase in volume be made twice as great as is necessary for condensation to result, a dense fog showing colours and settling slowly is produced.

Second Form of Apparatus.

The apparatus already described was not suitable for experiments upon pure gases, on account of the large volume of water present.

To remove all the dissolved gases from so large a quantity of water would have been very difficult.

Another reason for changing the form of the apparatus was that I wished to investigate in what way the number of drops produced depended upon the degree of supersaturation reached. It appeared, from the experiments already made, that the drops remained comparatively few with expansions considerably greater than that required to cause condensation to begin, and over a considerable range there was no appreciable increase in the number with increasing expansion. Yet, with very large expansions, the number was very great, and the drops sufficiently small to produce a coloured fog which settled very slowly.

The first apparatus was not convenient for making measurements with very large expansions, so no attempt was made to investigate with it whether there was a sudden transition from the one form of condensation to the other. It was thought that another form of apparatus would be more suitable for the purpose.

A very rapid expansion is evidently required for this investigation. For, let us consider one cubic centimetre of saturated air which is expanded rapidly. If we suppose the effect of the walls to be negligible, the ordinary equation for the cooling of a gas by adiabatic expansion may be applied to find the lowering of temperature and the resulting supersaturation till the volume amounts to 1·252 centims. At this stage, as we have seen, condensation begins upon a comparatively small number of scattered nuclei. There must at once result from the initial condensation a simultaneous loss of vapour and rise of temperature in the region immediately surrounding each incipient drop. The subsequent growth of the drop must be more or less gradual, being the result of the comparatively slow processes of diffusion and heat conduction.

If the expansion be slow, the supersaturation can nowhere greatly exceed that required for the formation of the first drops.

With very sudden expansions, however, even if they be much greater than that required to produce rain-like condensation, the drops which are the first to begin to form will not have time to grow sensibly before the expansion is completed, and their influence on the temperature and vapour contents of the air will be confined to a very small region round each. In that case the lowest temperature and maximum supersaturation reached throughout the greater part of the moist air will be the same as that calculated on the assumption that no condensation takes place.

The more numerous the drops, the shorter must the time taken in expansion be made, in order that there should be no sensible error due to the formation of the drops commencing before the expansion is completed.

Now the time of expansion can be made shorter in a small machine. The new expansion apparatus was therefore made upon quite a small scale, the effect of the reduced dimensions in increasing the error due to the walls being counterbalanced by the great reduction in the time of expansion.

The expansion ought evidently to be made most rapid just before it is completed, since it is just in the later stages of the expansion that drops are being formed, and we wish to reduce, as far as possible, their chance of growing appreciably before the expansion is completed. This end was kept in view in designing the apparatus.

The expansion apparatus (fig. 2), is made wholly of glass, to reduce the risk of contamination of the gas under investigation. This is contained in the space A under a pressure of from 20 to 40 centims. of mercury above that of the atmosphere. This expansion chamber A, is bounded below by the hollow-glass piston P, which is ground down so that it just slides freely in the outer tube.

There is, as indicated in the figure, an annular constriction on the latter. Into this the lower end of the piston has been ground with fine emery, so that, with no other lubricant than water, it prevents the gas in A escaping, even when the excess of pressure above is half an atmosphere or more.

The lower end of the tube is conical, with a circular aperture about 1 centim. in diameter, closed by a glass plug G. The grinding here, too, has to be sufficiently thorough to enable a pressure of two atmospheres to be maintained above it for several minutes without leakage, with only one or two drops of water to serve as lubricant.

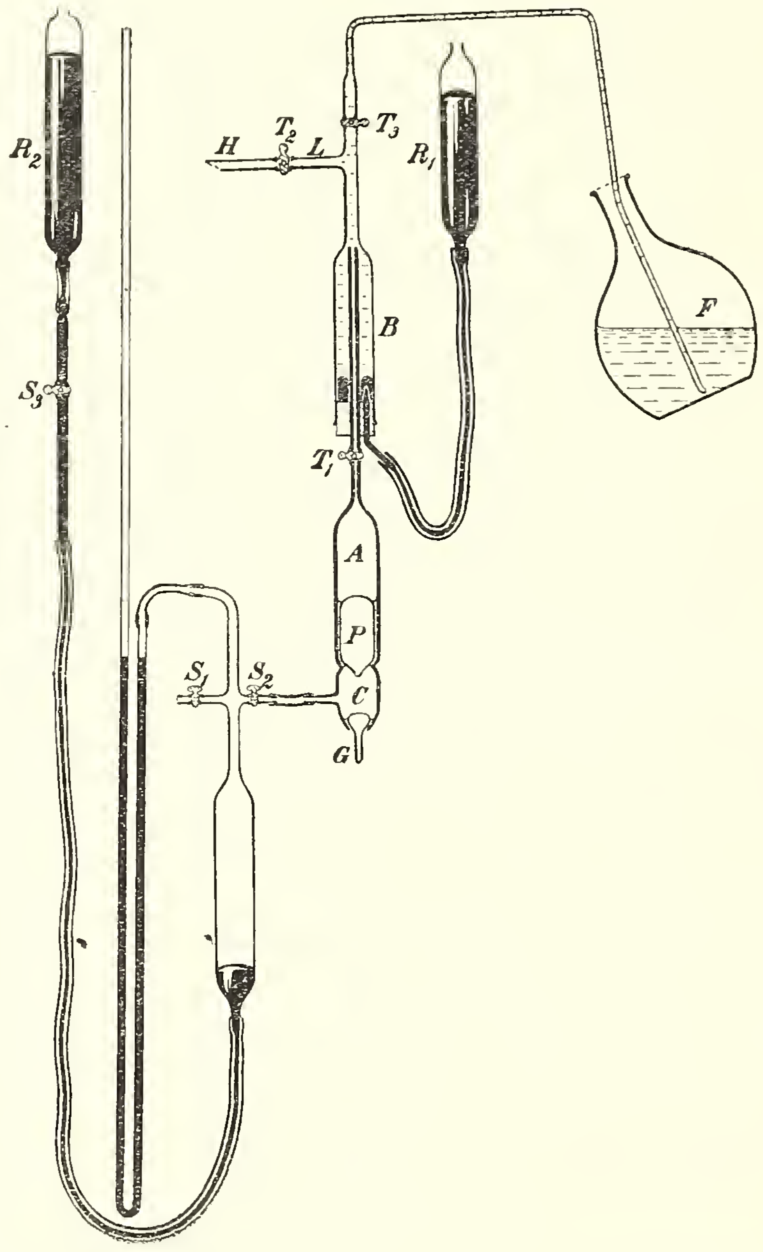
The upper end of the tube is drawn out and joined to a narrow-bore tube provided with a stopcock T_1, serving for the introduction of the gas and water.

When the apparatus is in use, the inner surface of A is covered with a film of water, which also fills the narrow space left between the piston and the walls of the tube.

By pumping air by means of the mercury pump on the left, into the space C below the piston, we can drive up the latter and so compress the gas in A to any extent we please. Then, on pushing up the plug G, we suddenly reduce the pressure in the small space C to that of the atmosphere, and the piston flies back to its original position, producing a sudden expansion of the gas in A.

After each expansion a small quantity of water is driven in through T_1. This serves to keep the walls of A covered with a film of water and to lubricate the piston. The greater part of it runs down and collects above the latter. When the piston is driven up again so that it is suspended freely in the tube, it gradually floats up through this water till it comes to rest with the water scarcely reaching above the straight part of its sides. In this way the water which lubricates the piston is continually being renewed, and the gradual contamination of the gas which would otherwise result by solution and diffusion of the air from below through the water is almost indefinitely retarded.

Fig. 2.



The machine used in nearly all the experiments described below was made from moderately thick-walled tubing, having an internal diameter of 2 centims. The expansion chamber A was between 4 and 5 centims. long, and had a capacity, when the piston was in its lowest position, of about 15 cub. centims. The cylindrical part of the piston was about 3 centims. in length.

The time required for the expansion to be completed must be very short. For the distance travelled by the piston was never so great as 2 centims., even with the greatest expansions used. To support the weight of the piston alone, required an excess of pressure below of 1 millim. of mercury. Now the driving pressure, even when the expansion was almost completed, was probably never less than 100 times as great as this. With the largest expansions used, when the piston had still to travel less than 2 centims., the initial driving pressure was more than an atmosphere, that is, about 760 times that required to balance the weight of the piston. This is on the assumption of an exceedingly rapid fall of pressure in the space below the piston when the plug G is driven up. If we make this assumption, the force driving the piston is always some hundreds of times its weight, and its initial acceleration some hundreds of time "*g*." Even an average acceleration of $100g$ would enable the 2 centims. to be travelled in about $\frac{1}{150}$ of a second.

Although the time taken may actually be considerably greater than this, these considerations are sufficient to show that it is likely to be exceedingly short.

Further, the piston must be moving with constantly increasing velocity till brought to a sudden stop at the constriction into which it fits.

The fact that contact takes place simultaneously over a considerable area, probably saves the tube from being broken by the blow it receives from the piston. The film of water which covers both surfaces, doubtless helps to break the shock. On two occasions, a machine was made only slightly larger than the one whose dimensions are given above, but in each case it was shivered by the impact almost the first time the piston was allowed to fly. More than one machine was useless, owing to the piston being driven so tightly home when the expansion was made, that all efforts failed to release it. To avoid this latter defect, it was found necessary to make the constriction a very sudden one. Great care has also to be taken to make it perfectly symmetrical; otherwise there is almost certain to be a space left between the piston and some part of the wall of the tube just above the constriction. In this, air-bubbles are apt to be entangled when the piston flies into the constriction. These may work their way up into A, and in addition they cause a splashing of the water by their momentary compression and subsequent expansion.

A supply of water for the lubrication of the piston is stored in the vessel B. The space over the mercury is completely filled with water up to the stopcocks T_2 and T_3, which remain closed throughout any series of experiments. By fixing the mercury reservoir R_1 at a sufficient height, the water in B is kept at a pressure high enough to drive it into A when the tap T_1 is opened. In this way the water is preserved from contamination with air, and only comes in contact with glass and mercury. It has been obtained free from dissolved gases by boiling distilled water rapidly down to about one-sixth of its bulk in the flask shown on the right. While it is boiling down, R_1 is repeatedly raised and lowered, to wash out any imprisoned air or unboiled water from B and the tube leading to the flask.

While the water is still boiling, B is filled by lowering R_1, a depth of about 1 centim. of mercury being, however, always left in B to prevent the water from coming in contact with the indiarubber stopper which closes the lower end of the tube. The tap T_3 is then closed and R fixed high enough to give the requisite pressure.

Introduction of the Gas.

The apparatus used in the preparation of the various gases was, in all cases, made entirely of glass, all joints being made with the blow-pipe. It was fused on to the end of the tube H (fig. 2). The methods of preparing the various gases are described later. The whole gas generating apparatus must first be filled with the pure gas up to the tap T_2, which is now kept closed.

Before introducing the gas into the expansion apparatus, A and B must first be filled with air-free water. This is done in the following way.

The piston P is drawn up to the top of A by opening the tap T_1 and lowering the mercury reservoir R_1, the other taps being closed. The gas which has collected in B is then driven out through T_3 by raising R_1 after closing T_1. Water is then drawn from the flask F, which is kept boiling the whole time, into B, and T_3 is closed. Again, T_1 is opened and water is introduced into A, driving the piston before it. A now contains water with a bubble of air at the top; this is driven into B by lowering R_1. The tap T_1 is closed, while the greater part of the water still remains in A, from which it slowly escapes by the floating up of the piston.

The small quantity of water which remains above the piston has, of course, been contaminated by contact with the air or other gas which originally occupied A. To replace it by pure water, B is first filled with air-free water as described in the last section. A small quantity of this is then passed into A while still hot, so that it floats above the cold water already there. It is, therefore, mainly the latter which flows away as the piston gradually rises. More water is run in from B before the piston quite reaches the top of A. This process is repeated two or three times, and finally the piston is driven right down to the bottom of A, which is thus completely filled with water. The tap T_1 is left open and R_1 raised to a considerable height, and the piston thus pressed down into the constriction so that the water does not escape.

When the apparatus has cooled, the piston is drawn up by lowering R_1, but is not allowed to rise quite to the top of A. There is very little risk of contamination by air at this stage, because the piston is slowly floating upwards, and the water filling the narrow space round the piston has therefore a comparatively great downward velocity. Diffusion of the air upwards through this water is thus prevented.

Then T_1 is closed, and some of the gas to be investigated drawn into B by lowering R_1 and opening T_2. It is then driven into A by opening T_1 and raising R_1, T_2 being closed. This pumping process is repeated till the pressure in A is rather in excess of what is required.

The gas which remains in B is driven out through T_3, which is then closed, and T_1 opened for a moment, so that the narrow-bore tube and stop-cock are filled with water. It is necessary, of course, for this purpose that R_1 should be raised high enough to overcome the pressure in A; it is, in fact, now kept permanently fixed at such a level throughout all subsequent operations.

The excess of water always remaining above the piston in A at this stage is now allowed to escape by applying sufficient pressure below to drive the piston up a little. The pressure is applied by pumping air into C, by means of the mercury compressing pump shown at the extreme left of the diagram. The plug G is then pushed up and the piston thus allowed to fly back into the constriction.

To prevent contamination of the gas, the glass taps T_1 T_2 T_3 are lubricated with water only. The only one which requires to be used after the above operations are completed is T_1. Since this is filled with water under considerable pressure, there is no danger of air gaining access through it.

Method of producing expansion of any desired amount.

With this apparatus, direct volume measurements were not made, but the relative volume change was deduced from measurements of the initial pressure, and the pressure exerted by the saturated gas at the same temperature when occupying the increased volume. The final volume v_2, being that of A when the piston is at the bottom, is always the same; and the corresponding pressure p_2 at the temperature of the room shows only comparatively small changes resulting from variations temperature, and from the solution of the gas by the small quantity of water which is run through the apparatus.

This final pressure p_2 was measured in the following way. A mark was made in the wall of A approximately on a level with the top of the piston, when this was in its lowest position.

A telescope was then fixed in a clamp about one metre off, and its height adjusted till the mark appeared to coincide with the top of the piston. By means of the compressing pump air was driven into C till the pressure was sufficient to drive up the piston a little. Then S_2 being left open and S_1 closed, the tap S_3, regulating the flow of mercury in the pump, was closed and the reservoir R_2 lowered and fixed in such a position that S_3 could be worked by the observer while looking through the telescope.

S_3 was then opened very slightly so that the mercury flowed very slowly through it into R_2 thus lowering the pressure in C. The slow descent of the piston was watched and S_3 closed just as the piston reached its zero position. The pressure in C as indicated by the open mercury pressure gauge was then read to the nearest millimetre.

To obtain the actual pressure in A we have to add to the pressure indicated by the gauge the barometer reading and to subtract the pressure required to support the weight of the piston. This last term enters as a constant correction which was determined combined with any constant error of the manometer, by noticing the pressure required to support the piston, when there was free communication between the inside of A and the atmosphere. At the same time the freedom of the apparatus from errors in the pressure-readings due to friction between the piston and the walls of the tube was tested by taking readings first while the piston was being raised and then while it was allowed to sink slowly down. No difference was detected.

To obtain any desired initial pressure in A, S_3 is opened, while R_2 is in its lower position in order to draw in air through S_1 which is then closed and S_2 opened, R_2 is then hung on a support fixed as high as can be conveniently reached, and S_3 is closed just as the pressure, as indicated by the manometer, reaches the desired amount. To make the expansion S_2 is closed and the plug G suddenly pressed up. The manometer is again read after expansion.

In the case of the more insoluble gases, when the temperature was steady, the measurement of the final pressure did not require to be determined after each expansion. Several expansions could under such conditions be made without any sensible change in the pressure measured when the piston was at the bottom of the tube.

In order that the rain-like condensation might be visible, the experiments were done in a dark room, and the same method of illumination was employed as in the case of the larger apparatus.

The glass, too, was kept clear inside by periodically removing the expansion apparatus and washing the inside with caustic potash and nitric acid and rinsing well with distilled water.

Temperature was measured by a mercury thermometer hung beside the expansion apparatus. This method is sufficiently accurate for the purpose, as the result of an expansion of a given amount was sensibly constant throughout the ordinary range of room temperature. It is necessary, however, that the temperature should be known sufficiently accurately to enable the vapour pressure to be found within the nearest millimetre of mercury. An error of half a degree in the temperature reading does not make a difference of much more than half a millimetre in the vapour pressure.

Calculation of v_2/v_1 from the Observations of Pressure.

To obtain the ratio of the final to the initial volume we have, when the gas present obeys BOYLE's law,

$$v_2/v_1 = P_1/P_2,$$

where P_1 is the pressure exerted by the gas alone before expansion, and P_2 is its pressure after expansion, when the temperature has risen to its former value.

Now

$$P_1 = p_1 + B - \pi - w,$$

and

$$P_2 = p_2 + B - \pi - w,$$

where p_1, p_2 are the pressures measured by the mercury gauge, before and after expansion, as already described, B is the atmospheric pressure, π is the maximum vapour pressure at the temperature of experiment, and w is the pressure required to balance the weight of the piston.

Results obtained with Air in the small Apparatus.

The same phenomena are observed as in the larger apparatus, as well as others to be described later.

After the removal of "dust" by repeated expansion, no condensation takes place within the moist air, unless v_2/v_1 exceeds a certain limit. With greater expansions rain-like condensation results. As will be seen from the following table, measurements of this critical value of v_2/v_1 made with the two machines give identical results, although the larger one contained twenty times as great a volume of air as the smaller. The expansion, therefore, appears to be sufficiently rapid to prevent the walls having any sensible effect.

EXPANSION required for Rain-like Condensation in Air.

Pressures all given in millims. of mercury. Correction for piston weight $w = 1$ millim.

	Date.	B.	t° C.	π.	p_1.	P_1.	p_2.	P_2.	$P_1/P_2 = v_2/v_1$.
1	February 13 . .	775	18·5	16	651	1409	372	1130	1·247
2	" 14 . .	775	17·5	15	685	1444	386	1145	1·261
3	" 17 . .	776	15·5	13	685	1447	392	1154	1·254
4	" 22 . .	764	16·5	14	602	1351	330	1079	1·252
5	" 22 . .	764	16·5	14	506	1255	254	1003	1·251
6	March 2 . . .	750	18·5	16	654	1387	377	1110	1·250
								Mean	1·252

The apparatus was charged with a fresh supply of air each day.

The results of all the measurements made with the small apparatus on the rain-like condensation are given in the table.

The expansion can be measured with quite as great accuracy as in the larger apparatus, but the whole number of drops when condensation first begins is inconveniently small in the small apparatus. This makes the measurements of the critical value of v_2/v_1 more troublesome.

Each determination of this requires a large number of observations to be made, p_1 being always made less or greater according as the previous expansion had brought down a shower or not. In this way it was possible, finally, to obtain the least value of p_1, necessary in order that a shower should result within about 2 millims.

It will again be noticed that the result obtained is with the limits of experimental error independent of the temperature between 15·5° and 18·5° C.

We may summarise the results of the measurements made with both machines upon the expansion required for rain-like condensation in the following statement.

When saturated air free from all extraneous nuclei is suddenly expanded, rain-like condensation takes place if the ratio of the final to the initial volume exceeds 1·252. This is true if the initial temperature is between 15° and 28° C.

It will be noticed that this expansion is less than that used by AITKEN in the experiments already referred to. The difference between the result of making the stroke of his pump slow or quick was therefore evidently due to the expansion not being quick enough to give the theoretical lowering of temperature.

Phenomena observed with Expansions greater than that required to produce Rain-like Condensation.

If a series of expansions be made of constantly increasing amount, the following phenomena are observed.

The drops are, if the expansion be only slightly greater than is sufficient to produce condensation, only few in number. More of them are seen if the expansion be somewhat greater, but even when v_2/v_1 is as great as 1·37, the condensation still takes the form of a shower of drops, which settle within a few seconds. To the eye there is no marked difference in the density of the shower over quite a wide range of expansions.

If, however, v_2/v_1 be increased from 1·37 to 1·38, the increase in the number of drops is so great that there is no longer any resemblance to a shower of rain, but a fog results, taking a minute or more to settle.*

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* [*Note added July 22nd*, 1897.—When expansion results in a fog, it is of course necessary to get rid of all traces of it before proceeding to a fresh observation. This was done by repeated expansions of moderate amount, as in the removal of the original dust particles.]

With expansions greater than this, the density of the fog appears to go on increasing with great rapidity as the expansion is increased. It is now convenient to remove the condensing lens and examine the fog by looking directly through it at the gas-flame. Coloured diffraction rings make their appearance when v_2/v_1 is about 1·38 and they increase rapidly in brilliancy and size as the expansion is made greater and greater.

Before v_2/v_1 reaches 1·40, the region within the first ring, which is whitish with smaller expansions, becomes brightly coloured. With greater expansions, the rings rapidly become so large that the colour corresponding to the central part of the field fills the whole tube.

The colour phenomena beyond this stage are surprisingly definite. They are best observed by looking through the cloud chamber slighly to one side of the source of light, which ought now to be made as bright as possible, and have a black background.

If v_2/v_1 be between 1·41 and 1·42, brilliant greens and blue-greens are seen. At about 1·42 there is a very rapid change from blue to red through violet. The violet appears only for a very small range of expansion, a change of one or two millimetres in the initial pressure being sufficient to complete the change from blue to red.

As the expansion is further increased, the colour passes from red through yellow to white. With expansions greater than about 1·44, the fog is always white with a greenish or bluish tinge.

The whole of these colour phenomena, it will be seen, are confined to quite a narrow range of expansions. Below 1·38 the drops are too large and few; and above 1·44 they appear to be too small to produce the colours.

Colours of exactly the same kind were obtained by KIESSLING[*] and by AITKEN[†] by expanding ordinary moist unfiltered air; but in the reverse order, pale yellow being the first to appear, followed with increasing expansions by a reddish colour, then by blue, and then green.

The explanation of the difference plainly, is that in their experiments the number of the drops was determined by the number of "dust" particles present, and increased expansion caused a larger quantity of water to condense on each particle.

Increasing the expansion thus increased the size of the drops. Now in the experiments here described, the greater the expansion, the smaller appear to be the resulting drops, which indicates that as the supersaturation is increased, a larger number of nuclei come into play, so that each receives a smaller share of the water which condenses.

Similar phenomena are exhibited by light transmitted through a steam-jet under certain conditions. They have been investigated by R. V. HELMHOLTZ,[*] AITKEN[†] and, in a more elaborate way, by BARUS.[‡]

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[*] GÖTTING., 'Nachr.,' 1884, p. 226.

[†] 'Proc. Roy Soc.,' vol. 51, p. 422, 1892.

Measurements of the Expansion required to produce Cloud-like Condensation.

The transition from rain-like to cloud-like condensation is sudden enough to enable one to measure, with considerable accuracy, the value of the ratio v_2/v_1 when cloud-like condensation just begins. There is, in fact, a second condensation point, below which the drops are few, and the number shows only a slight increase with increasing expansion; while above it the number increases at an excessively rapid rate with increasing expansion.

EXPANSION required for Cloud-like Condensation in Saturated Air.

Date.	B.	t° C.	π.	p_1.	P_1.	p_2.	P_2.	$P_1/P_2 = v_2/v_1$.	Result.
February 14. .	775	17·5	15	706	1465	308	1067	1·373	Rain
„ 14. .	775	17·5	15	712	1471	308	1067	1·378	Fog
„ 15. .	775	18·5	16	791	1549	369	1127	1·375	Rain
„ 15. .	775	18·5	16	795	1553	369	1127	1·378	Fog
„ 18. .	769	15·0	13	803	1558	381	1136	1·372	Rain
„ 18. .	769	15·0	13	813	1568	381	1136	1·380	Fog

The transition from rain to fog takes place when v_2/v_1 is between 1·37 and 1·38.

The above results were obtained using the same method of illumination as in the experiments on rain-like condensation. Observations were also made with the condensing lens removed.

FIRST Appearance of Diffraction Rings.

Date.	B.	t° C.	π.	p_1.	P_1.	p_2.	P_2.	$P_1/P_2 = v_2/v_1$.
February 24	776	15	13	676	1438	279	1041	1·381
„ 25	772	13	11	667	1427	277	1037	1·376
March 2	750	18	15	807	1541	380	1114	1·383
„ 2	750	18·5	16	715	1448	318	1051	1·378
							Mean .	1·379

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[*] 'Wied. Ann.,' 32, p. 1, 1887.

[†] 'Proc. Roy. Soc.,' vol. 51, p. 422, 1892.

[‡] BARUS, *loc. cit.*, also 'Phil. Mag.,' vol 35, p. 315, 1893.

Observations were also made of the time taken by the drops to settle, as v_2/v_1 was gradually increased. This was of course very short when the condensation took the rain-like form. It showed a very sudden increase when the rain was replaced by fog. For example, such measurements were made in connection with the last observation given in the preceding table.

v_2/v_1.	
1·378	Colours scarcely visible, drops settled in a few seconds.
1·381	Rings faint, drops took about one minute to settle.
1·385	Rings brilliant, took several minutes to settle.

All these methods of making evident the change from rain to fog agree in showing that this takes place when v_2/v_1 lies between 1·37 and 1·38.

Colour Observations.

The colour phenomena change so rapidly as v_2/v_1 is increased from 1·38 to 1·40 that consistent measurements were not possible. In the tables which follow the observations therefore begin where the brilliant greens previously referred to first appear. The colours are those seen on looking through the tube, almost, but not quite in the direction of the source of light.

February 25. $t = 13°$ C.		March 3. $t = 18°$ to $19°$ C.	
v_2/v_1.	Colour.	v_2/v_1.	Colour.
1·408	Brilliant green	1·410	Green
1·408	" "	1·410	"
1·412	" "	1·413	"
1·414	" "	1·416	Blue-green
1·414	" "	1·418	Brilliant blue
1·419	Blue-green	1·419	Violet
1·419	Purple	1·420	"
1·422	"	1·420	Reddish-purple
1·424	Brilliant red	1·426	Red
1·426	Red	1·429	Reddish-yellow
1·428	"	1·436	Yellowish-white
1·429	"	1·448	White
1·434	Reddish	1·469	Greenish-white
1·437	Reddish-white		
1·453	Greenish-white		
1·458	" "		

When the greenish-white fog appeared, the colour was the same from whatever point the tube was viewed, out of the direct line of the incident light. The particles are then evidently small enough to scatter the red light less than the blue.

Meteorological Applications.

The question of the degree of supersaturation reached in these experiments is postponed till the results obtained with other gases have been given. In considering the meteorological applications we are directly concerned with the expansion required to cause condensation in air originally saturated. For adiabatic expansion to result in condensation in saturated air free from all foreign nuclei, we have seen that the final volume must exceed 1·252 times the initial volume.

To obtain the corresponding ratio between the final and initial pressures we have

$$p_1 v_1^{\gamma} = p_2 v_2^{\gamma},$$

or

$$\frac{p_2}{p_1} = \left(\frac{v_1}{v_2}\right)^{\gamma}.$$

where γ is the ratio of the specific heat of air at constant pressure to that at constant volume. The difference in γ for dry and moist air is small, and may here be neglected, γ being therefore taken as equal to 1·41.

Now

$$\frac{v_1}{v_2} = \frac{1}{1{\cdot}252}, \quad \text{therefore} \quad \frac{p_2}{p_1} = \frac{1}{1{\cdot}252^{1{\cdot}41}} = {\cdot}728.$$

Condensation must therefore take place in air free from foreign nuclei when the pressure is reduced adiabatically to ·728 of the value which it has when the air is just saturated. The drops which are formed are, as we have seen, comparatively few. The fall of pressure required is sensibly the same for all values of the initial temperature between 28° and 15° C., and it is therefore probable that the result may be applied to considerably lower temperatures without any great error.

It is natural to suppose that when there is an upward current of moist air, the foreign nuclei will be left behind through becoming loaded with the water which condenses on them, and that the air which rises above the lower cloud layer thus formed will be dust-free and supersaturated.

It follows from the results of these experiments that condensation will again begin when the air reaches such a height that the pressure is reduced to about ·73 of that at the upper surface of the lower cloud.

It is not likely that the cloud-like condensation obtained with greater expansion has any meteorological significance. For it is unlikely that there can ever be such a sudden uprush of air as to enable any great degree of supersaturation to be maintained when drops have already begun to form.

Oxygen.

Preparation.—Potassium permanganate was heated in a small glass tube fused on to H (fig. 2). This was exhausted and then heated till the pressure considerably exceeded that of the atmosphere, and the process of alternate exhaustion and heating many times repeated.

The mercury reservoirs B, R_1 with the taps T_2, T_3 served as a pump.

Results.—Oxygen behaves exactly like air in these experiments. The expansion required to produce both rain-like and cloud-like condensation, is practically the same in both. The colour phenomena are also exactly alike.

EXPANSION required to produce Rain-like Condensation in Saturated Oxygen.

Pressures all given in millimetres of mercury. Correction for piston weight, $w = 1$ millim.

Date.	B.	t° C.	π.	p_1.	P_1.	p_2.	P_2.	$P_1/P_2 = v_2/v_1$.
May 8	769	17	14	594	1348	318	1072	1·258
,, 14	768	20	17	638	1388	357	1107	1·254
,, 15	768	21	18	579	1328	307	1056	1·258
							Mean	1·257

A fresh supply of oxygen was used each day.

EXPANSION required to produce Cloud-like Condensation in Oxygen.

	Date.	B.	t° C.	π.	p_1.	P_1	p_2.	P_2.	$P_1/P_2 = v_2/v_1$.
	May 9	769	18·0	15	732	1485	318	1071	1·386
1	,, 14	767	20·5	18	659	1407	273	1021	1·378
2	,, 14	766	21·5	19	665	1411	273	1019	1·385
								Mean	1·383

Measurements were also made of the ratio v_2/v_1 when the colour produced by the expansion was the sensitive tint between the blue and red referred to in the account of the colour phenomena observed in the experiments with air.

EXPANSION required to produce the Sensitive Tint.

Date.	B.	$t°$ C.	π.	p_1.	P_1.	p_2.	P_2.	$P_1/P_2 = v_2/v_1$.	Colour.
March 6 . .	752	19·5	17	804	1538	347	1081	1·423	Violet
„ 7 . .	775	17·5	15	799	1558	341	1100	1·417	„
							Mean	1·420	

Carbonic Acid.

Preparation.—Potassium bicarbonate was heated in a glass tube, fused directly to H. This was repeatedly heated and pumped out.

Results.—Carbonic acid shows, like air and oxygen, the two kinds of condensation, each requiring a definite minimum expansion for its production.

The measurements could not be made with the same accuracy in this case on account of the solubility of the gas in water. This caused a continual falling off in the pressure, necessitating the reading of the final pressure p_2 after each expansion.

On account of the difference in γ, the results with CO_2 are not directly comparable with those obtained with air, the same expansion corresponding to a different fall of temperature.

The colour phenomena were not looked for.

In the table which follows, the pressure readings corresponding to the greatest expansion which was made without condensation, as well as those of the least expansion which resulted in condensation, are given. In the case of the more insoluble gases, the difference between these only amounted to 2 millims.; here, as will be seen, it is considerably greater.

RAIN-LIKE Condensation in CO_2.

Date.	B.	$t°$ C.	π.	p_1.	P_1.	p_2.	P_2.	P_1/P_2.	Result.
May 23	764	19	16	710	1457	333	1080	1·349	0
„	764	19	16	700	1447	314	1061	1·364	Rain
May 25	775	17	14	605	1355	247	997	1·359	0
„	775	17	14	612	1362	245	995	1·369	Rain
May 25	775	17	14	599	1349	242	992	1·360	0
„	775	17	14	603	1353	240	990	1·367	Rain

Condensation begins when P_1/P_2 is between 1·36 and 1·37.

For pressure changes within these limits (between $1\frac{1}{2}$ and 2 atmospheres) BOYLE'S law is sufficiently nearly obeyed to justify us in saying that condensation begins when v_2/v_1 lies between 1·35 and 1·37. REGNAULT found* that if the pressure of the CO_2 was changed from 1 atmosphere to 2, the ratio of the initial to the final volume was 2 × 1·0076. The difference between P_1/P_2 and v_2/v_1 is therefore well within 1 per cent.

CLOUD-LIKE Condensation in CO_2.

Date.	B.	$t°$ C.	π.	p_1.	P_1.	p_2.	P_2.	P_1/P_2.	Result.
May 25.	775	17·5	15	738	1487	223	972	1·530	Rain
"	775	17·5	15	734	1503	230	979	1·535	Fog

All the above results were obtained with the same sample of CO_2. On absorbing the gas by KOH a bubble amounting to less than 1 part in 1000 of the whole remained. The gas had been in the expansion apparatus for three days and 50 expansions had been made. The contamination which takes place by air diffusing through the lubricating water round the piston is therefore certainly very slight. In the experiments with CO_2 the lubricating water was less frequently renewed, and a smaller quantity run in at a time than with the less soluble gases. There was, therefore, even less chance of contamination of the latter than of the CO_2.

Hydrogen.

This was prepared by passing steam over sodium. This method was used by SCOTT in his experiments on the composition of water.†

The apparatus for the preparation of the gas is shown in fig. 3.

The water was contained in the bulb A and the sodium in B, which was prolonged into a narrower tube C, fused directly to H in fig. 2. The vertical tube D served for the introduction of the water.

The sodium was previously heated in a tube, kept exhausted by the water pump. The tube was held for several minutes in a Bunsen flame, and the sodium then poured off into the clean part of the tube.

The water to be introduced into A was obtained free from dissolved gases by boiling rapidly down in a flask to about one-sixth of the original volume. This was drawn up through D without allowing it to cool, the end of D dipped under mercury and the apparatus immediately pumped out. The mercury rose in D, which now served as pressure-gauge and safety-tube.

The bulb A was now warmed till the pressure exceeded that of the atmosphere, and bubbles began to escape through the mercury in E.

The flame was then removed, and the apparatus again pumped out to as low a pressure as possible. Hydrogen was thus generated and pumped out several times, and lastly a vigorous stream of hydrogen was allowed to escape through the water in the flask F (fig. 2) by opening the taps T_2 and T_3. The flame was then removed and T_2 closed, the gas which still continued to come off escaping through the safety-tube D. The hydrogen was then ready to be pumped into the expansion apparatus as required. Even in the cold, hydrogen is slowly formed by the water vapour reaching the sodium by diffusion, and escapes through the safety-tube. No further heating was therefore required when a fresh charge was wanted in the expansion apparatus.

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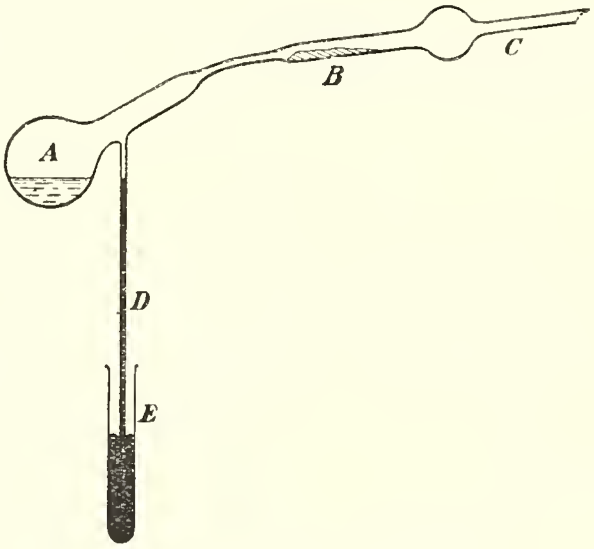
* 'Comptes Rendus,' vol. 23, p. 794 (1846).

† 'Phil. Trans.,' 1893, p. 543.

Results.—The phenomena attending condensation in presence of hydrogen differed considerably from those observed with other gases.

As in air and oxygen, dense condensation begins when v_2/v_1 is between 1·37 and 1·38, and the number of particles rapidly increases with increasing expansion. With very slightly smaller expansions, however, the drops are excessively few, and if v_2/v_1 be less than 1·36, they are either absent altogether or at the most one or two scattered drops are seen. It was found impossible to get any consistent measurements of the minimum expansion required to make these drops appear. In no case was any condensation at all observed when v_2/v_1 was less than 1·30, while in one series of observations no condensation resulted when v_2/v_1 was as great as 1·356.

Fig. 3.



It is likely that this irregular condensation is due to impurities in the gas. For the observations in which no condensation whatever was observed, even when v_2/v_1 was not much below 1·36, were all made when the hydrogen was comparatively fresh, before it had been allowed to expand more than a very few times. The slight contamination which may take place by diffusion of air through the water lubricating the piston may account for their subsequent appearance. The contamination which can take place in this way must, as has been shown, be very slight; but it is quite possible that an exceedingly small trace of air would be sufficient to cause the slight condensation which is observed. It must be remembered that even if only one drop separates out it will be seen. Colours like those observed in the other gases made their appearance when the expansion exceeded that required to produce the dense condensation. Measurements, however, were not made of the expansion required to produce a given colour.

Expansion required to produce Dense Condensation in Hydrogen.

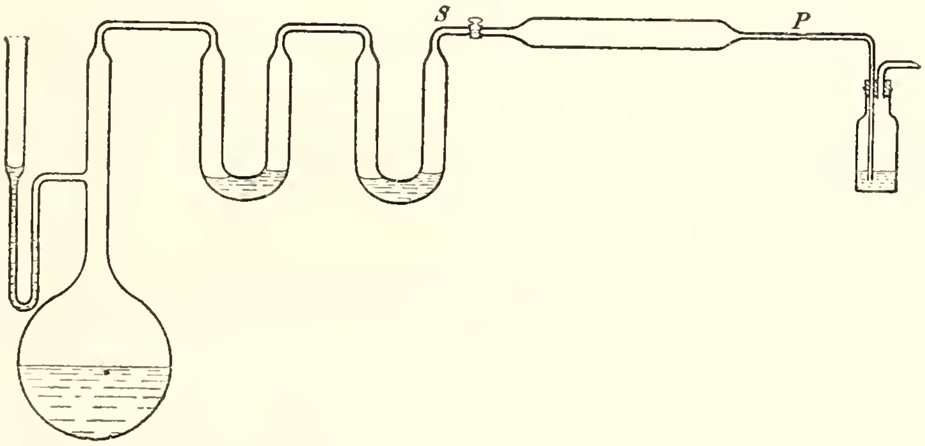
Date.	B.	$t°$ C.	π.	p_1.	P_1.	p_2.	P_2.	$P_1/P_2 = v_2/v_1$.
Aug. 4	763	22·0	20	670	1412	283	1025	1·378
„ 6	767	20·5	18	661	1409	267	1015	1·388
„ 6	767	21·0	18	652	1400	269	1017	1·377
„ 6	767	21·0	18	653	1401	269	1017	1·378
							Mean	1·380

Chlorine.

This was prepared by heating hydrochloric acid with potassium bichromate.

The apparatus is shown in fig. 4. The U-tubes contained water. A supply of the gas was collected in the tube SP, by allowing a rapid stream to pass for about three-quarters of an hour, and then closing the stopcock, and sealing off at P with the blow-pipe.

Fig. 4.



The tube was then cut at S. The part from S to P was then removed, and the open end joined to L (fig. 2) in place of the stopcock T_2. The chlorine was then pumped into the expansion apparatus when required, the reservoir B (fig. 2) with the tubes connected to it being of course first completely filled with well-boiled water. The tube SP was throughout protected from the light by a wrapping of black paper.

After use, the chlorine was absorbed by driving KOH into the expansion chamber. (This was done by expelling the water from B, and drawing in potash in its place, and then opening T_1, while R_1 was raised sufficiently high to overcome the pressure in A.) The bubble which remained was then drawn up into the capillary tube for measurement.

Out of the three samples of chlorine used, two were analysed in this way. In both cases the volume of gas unabsorbed amounted to between 1 and 2 parts in 1000 of the whole.

Results.—Chlorine shows both kinds of condensation, each requiring a definite minimum expansion. With expansions greater than was necessary to produce cloud-like condensation, colour phenomena were observed like those exhibited by air and oxygen.

The solubility of the chlorine introduced difficulties of the kind experienced with CO_2, interfering considerably with the exactness of the measurements. The final pressure p_2 had to be measured after each expansion, no water being run in till after this measurement was completed.

The drops when the condensation was of the rain-like form appeared to the eye to be much more numerous in chlorine than in the other gases.

EXPANSION required to produce Rain-like Condensation in Chlorine.

Date.	B.	$t°$ C.	π.	p_1.	P_1.	p_2.	P_2.	P_1/P_2.	Result.
August 20 . .	761	21·5	19	443	1184	166	907	1·306	Rain.
,, 20 . .	761	21·5	19	420	1161	153	894	1·299	0
August 24 . .	760	20	17	560	1302	257	999	1·304	Rain.
,, 24 . .	760	20	17	549	1291	252	994	1·299	0

Rain-like condensation begins when P_1/P_2 is about 1·30.

EXPANSION required to produce Cloud-like Condensation in Chlorine.

Date.	B.	$t°$ C.	π.	p_1.	P_1.	p_2.	P_2.	P_1/P_2.
August 28	768	18	15	741	1490	280	1029	1·448
,, 28	768	18	15	660	1409	223	972	1·449

Cloud-like condensation begins when P_1/P_2 is about 1·45. The second observation was made with the condensing lens removed, the readings given being those corresponding to the least expansion required to make coloured rings appear. With greater expansions the size and brilliancy of the rings rapidly increased.

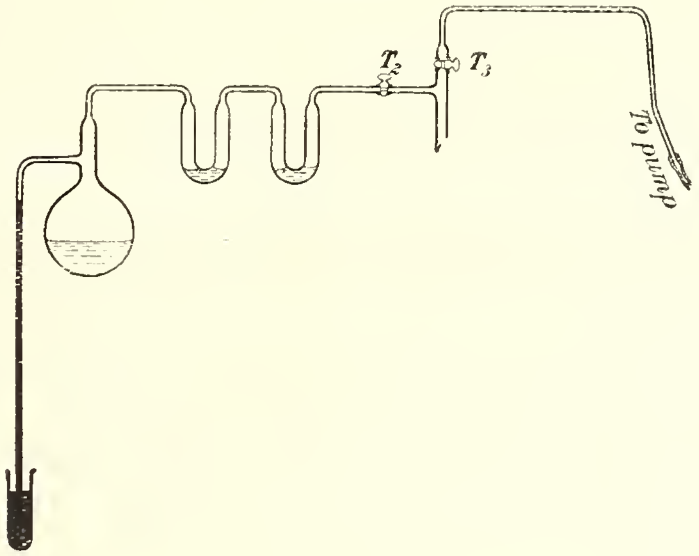
We cannot suppose that chlorine at the pressures and temperatures used in these experiments obeys BOYLE's law even approximately. It is not allowable, therefore, to put $P_1/P_2 = v_2/v_1$.

Nitrogen.

This was prepared by adding ammonium chloride to a nearly saturated solution of sodium nitrite, till no more would dissolve, and warming gently. In the first series of experiments a concentrated solution of potassium bichromate was added. This was omitted in the later experiments. The gas was allowed to pass through two U-tubes containing strong caustic potash solution.

The apparatus for the preparation of the gas is shown in fig. 5.

Fig. 5.



The liquid was drawn into the flask through the vertical tube. This was then made to dip below the surface of mercury contained in a small test-tube. The apparatus was then connected to the water-pump, and the liquid in the flask allowed to boil under very low pressure, by warming gently. This was allowed to continue for some time. The tap T_2 was then closed, and the heating continued till the pressure exceeded that of the atmosphere and the nitrogen began to escape through the safety-tube. T_2 was then again opened and the gas allowed to escape through T_2 and T_3. The temperature of the flask was never allowed to rise more than was sufficient to give a steady stream of the gas, which gradually ceased after the removal of the flame. Finally T_2 was closed and the heating discontinued. The nitrogen could then be pumped out when required.

Results.—The results are practically identical with those obtained with air and oxygen.

The experiments of October 6 were made with the same expansion apparatus as had been used with the other gases. This was unfortunately broken immediately afterwards and the apparatus made to replace it was much smaller, having a capacity of only 8 cub. centims., the length of the expansion chamber being 4 centims., and that of the piston 5 centims. The pressure required to balance the weight of the piston was about 2 millims. of mercury. The volume of the gas is, therefore, smaller, and the rate at which it expands slower than in the former machine.

EXPANSION Required to Produce Rain-like Condensation in Nitrogen.

Date.	B.	$t°$ C.	π.	p_1.	P_1.	p_2.	P_2.	$P_1/P_2 = v_2/v_1$.
October 6	754	13	11	681	1423	390	1132	1·257
November 19	765	17·5	15	562	1310	289	1037	1·263
„ 19	764	17	14	546	1294	276	1024	1·264
„ 19	764	17	14	540	1288	275	1023	1·259
November 30	772	11	10	610	1370	321	1081	1·267
							Mean	1·262

The number of drops appeared to be small in nitrogen.

EXPANSION Required to Produce Cloud-like Condensation in Nitrogen.

Date.	B.	$t°$ C.	π.	p_1.	P_1.	p_2.	P_2.	$P_1/P_2 = v_2/v_1$.
October 6	754	13·5	12	765	1506	350	1091	1·380
November 21	775	15·0	13	713	1473	307	1067	1·380
„ 21	775	15·0	13	709	1469	304	1064	1·381
							Mean	1·38

The colour phenomena were exactly like those observed in air.

Measurements were made of the expansion required to produce the sensitive tint.

Date.	$t°$ C.	v_2/v_1.
October 6	13·5	1·417
November 28.	11·5	1·434
„ 28.	11·5	1·430
	Mean	1·427

The observations of November 28 were made with the smaller machine, those of October 6 with that which had been used for the experiments on the other gases.

Supersaturation Resulting from a Given Expansion.

By the supersaturation is here meant the ratio of the actual density of the vapour when the expansion has just been completed, and the minimum temperature has therefore been reached to the density of vapour which is in equilibrium over a flat surface of water at that temperature.

It is assumed in what follows that the expansion is completed before any appreciable amount of water has had time to condense on the walls, or in drops throughout the moist gas.

To find the lowest temperature reached we have the well-known equation for the cooling of a gas by adiabatic expression,

$$\frac{\theta_2}{\theta_1} = \left(\frac{v_1}{v_2}\right)^{\gamma-1},$$

where θ_1, θ_2, are the initial and final absolute temperatures, and γ is the ratio of the specific heat at constant pressure to that at constant volume. This has been assumed below to be the same as in the dry gas, the effect on γ of the small quantity of vapour present being neglected. The error introduced in this way, as pointed out by R. v. HELMOLTZ,[*] is inappreciable at temperatures below 30° C.

Knowing θ_1 and v_2/v_1, the ratio measured in these experiments, we can, therefore, calculate θ_2.

Let π_1, π_2 be the pressure of saturated vapour over a flat surface of water at the temperature θ_1, θ_2 respectively. π_1 is then the initial pressure of the vapour before expansion. The volume of the vapour is suddenly changed from v_1 to v_2. We cannot, however, calculate the resulting change in its pressure, there being no reason to suppose that BOYLE'S law is even approximately obeyed by the highly supersaturated vapour. There is no such uncertainty, however, as to the density of the vapour, which must change inversely as the volume. It is for this reason that the supersaturation is here defined as the ratio of the actual to the equilibrium density over a flat surface, and not in terms of the corresponding pressure.

The supersaturation, according to the above definition, is equal to

$$S = \rho'/\rho_2,$$

where ρ' is the final density of the vapour before condensation takes place, and ρ_2 is the density of the saturated vapour at the temperature θ_2.

But $\frac{\rho'}{\rho_1} = \frac{v_1}{v_2}$, therefore, $S = \frac{\rho_1}{\rho_2} \times \frac{v_1}{v_2}$.

Now the actual density of saturated water vapour in the presence of air at ordinary atmospheric temperatures, has been shown by SHAW[†] to agree very closely with the density calculated on the assumption that the vapour behaves like a perfect gas. We may, therefore, write

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[*] 'Wied. Ann.,' xxvii., p. 508 (1886).

[†] 'Phil. Trans.,' 1888, A, p. 83.

$$\frac{\rho_1}{\rho_2} = \frac{\pi_1}{\pi_2} \times \frac{\theta_2}{\theta_1}.$$

$$\text{Therefore, } S = \frac{\pi_1}{\pi_2} \times \frac{\theta_2}{\theta_1} \times \frac{v_1}{v_2} = \frac{\pi_1}{\pi_2} \times \left(\frac{v_1}{v_2}\right)^{\gamma}.$$

Supersaturation Required for Rain-like Condensation.

For convenience of comparison the calculations have been made for the case where the initial temperature t_1 is 20° C. As we have seen, the ratio v_2/v_1 when condensation just begins, is within the limits of experimental error, constant within the ordinary range of room temperature.

Chlorine is too far removed from the condition of a perfect gas for the fall of temperature to be calculated. The error from the same cause may also be considerable in the case of CO_2.

In the following table REGNAULT's numbers have been used for the vapour pressure at temperatures above the freezing point. The vapour pressures over water below the freezing point are from a paper by JUHLIN,* who has measured directly the pressure over water over a considerable range of temperature below the freezing point. t_1, t_2 are the initial and final temperatures Centigrade, $\theta_1 = t_1 + 273$, $\theta_2 = t_2 + 273$.

	θ_1.	π_1.	v_2/v_1.	γ.	θ_1/θ_2.	t_2.	π_2.	$S = \frac{\pi_1}{\pi_2}\left(\frac{v_1}{v_2}\right)^{\gamma}$.
Air	293	17·39	1·252	1·41	1·097	− 5·8	3·02	4·2
Oxygen	293	17·39	1·257	1·41	1·098	− 6·2	2·93	4·3
Nitrogen	293	17·39	1·262	1·41	1·100	− 6·7	2·83	4·4
Carbonic Acid . .	293	17·39	1·365	1·31	1·101	− 6·9	2·78	4·2
(Chlorine . . .	293	17·39	1·30	1·32	1 087	− 3·5	3·58	3·4)

Hydrogen does not appear in this table, as no regular rain-like condensation was observed.

It will be noticed that the supersaturation required to cause condensation is practically the same in CO_2 as in the other gases, in spite of the great difference in v_2/v_1.

The supersaturation is in each case the greatest which can exist at the temperature t_2° C. without condensation resulting.

To find to what extent this depends upon the temperature, we may make use of the fact that v_2/v_1, when the resulting supersaturation is just sufficient to cause condensation, is in the case of air constant for temperatures between 15·5° C. and 28·8° C.

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* 'Bihang till K. S. Vet. Akad. Handlingar,' Bd. 17.

SUPERSATURATION required to cause Condensation in air at different temperatures.

t_1.	θ_1.	π_1.	v_2/v_1.	γ.	θ_1/θ_2.	t_2.	π_2.	$S = \frac{\pi_1}{\pi_2}\left(\frac{v_1}{v_2}\right)^\gamma$.
15·5	285·5	13·12	1·252	1·41	1·097	− 10	2·197	4·35
20°	293	17·39	1·252	1·41	1·097	− 5·8	3·02	4·2
28·8	301·8	29·45	1·252	1·41	1·097	+ 2·2	5·377	4·0

Thus the maximum supersaturation is 4·35 at − 10° C. and 4·0 at + 2·2° C. It therefore diminishes with rising temperature at the rate of about ·03 per degree.

Supersaturation required to produce Cloud-like Condensation.

The calculations are again made for an initial temperature of 20° C.

The results for Air, Oxygen, Hydrogen, and Nitrogen are grouped together, the difference in the observed value of v_2/v_1 when the dense condensation begins being no greater than can be accounted for by experimental errors. In all these gases the least value of v_2/v_1 when the condensation first becomes cloud-like is about 1·38. In air, however, in which more exact measurements were attempted, the beginning of the change from the rain-like to the cloud-like form could be detected when v_2/v_1 only slightly exceeded 1·37.

The calculations have therefore been made taking $v_2/v_1 = 1·375$. $t_1 = 20°$ C.

	θ_1.	π_1.	v_2/v_1.	γ_1.	θ_1/θ_2.	t_2.	π_2.	$S' = \frac{\pi_1}{\pi_2}\left(\frac{v_1}{v_2}\right)^\gamma$:
Air, O, H, N . .	293	17·39	1·375	1·41	1·140	− 15·8	1·41	7·9
CO_2	293	17·39	1·53	1·31	1 141	− 16·2	1·37	7·3
(Chlorine . . .	293	17·39	1·44	1·32	1·124	− 12·3	1·83	5·9)

If then by sudden cooling a supersaturation exceeding 7·9 be produced at a temperature of about − 16° C., the condensation, instead of taking place on a small number of scattered nuclei, as with a smaller degree of supersaturation, takes place upon a very large number, the number of nuclei which come into play increasing at a very rapid rate with increasing expansion. It will be noticed that the supersaturation required to produce either kind of condensation is practically the same in all gases, the rain-like condensation, however, being absent in hydrogen.

Supersaturation required to produce the sensitive tint.

At first sight it might seem that when the expansion is so great that a very large number of drops begin to grow before it is completed, the maximum supersaturation must be much less than is obtained by calculation according to the above method. It is difficult, however, to understand the constancy of the results obtained in the observations of the colour phenomena unless the supersaturation resulting from expansion of a given amount is always the same in spite of the variations which there must be in the rate of expansion. If the maximum supersaturation be independent of variations in the rate of expansion, it must be because the maximum supersaturation reached does not differ much from what would result from an infinitely rapid expansion.

This is, perhaps, not very surprising if we consider how little time the drops have to grow before the expansion is completed. To produce the sensitive tint in air v_2/v_1 must be made equal to 1·420. It is only while v_2/v_1 is increasing from 1·38 to 1·42, that the number of drops in process of formation is at all considerable, that is, when the piston has already completed nine-tenths of its journey. Now the piston must be moving with constantly increasing velocity; the whole distance moved by the piston amounts to less than 1·5 centimetres; the time taken to travel the last tenth of this, that is, less than 1·5 millimetres, must therefore be very short. We have seen that the time taken to travel the whole distance is itself very short. The growth of the drops too, as has already been pointed out, cannot be very rapid. It is quite likely therefore that even when they are very numerous, the quantity of water which separates out upon them before the expansion is complete may be too small to diminish appreciably the final supersaturation reached.

The supersaturation required to produce the sensitive tint in air is calculated below.

t_1.	θ_1.	π_1.	v_2/v_1.	γ.	θ_1/θ_2.	t_2.	π_2.	$S = \frac{\pi_1}{\pi_2}\left(\frac{v_1}{v_2}\right)^\gamma$.
20°	293	17·39	1·420	1·41	1·155	– 19·2	1·07	9·9

On the number of the drops.

It is possible to obtain some information as to the number of the drops formed for a certain range of supersaturation from the colour phenomena. For from the colours we ought to be able to deduce the size of the full-grown drops, and the total quantity of water which condenses in consequence of the corresponding expansion may be calculated. With the exceedingly dense fogs with which we are now dealing there is no doubt that the water which condenses on the walls will be small in quantity compared with what condenses in the form of drops. From the quantity of water which separates, and the size of the drops, we may calculate the number, assuming the water to be equally divided among them.

It is assumed here that the cloud-particles are actually liquid drops and not ice-crystals, in spite of the fact that the condensation begins at temperatures much below the freezing point, and that the temperature when the particles are full grown is, as we shall see, also slightly below the freezing point.

Let us consider first the quantity of water which separates out in consequence of an expansion of a given amount. Let us suppose the expansion to be completed before the drops have grown to more than a very small fraction of their final size, so that the theoretical lowering of temperature results. Let t_1 be the temperature Centigrade before expansion, t_2 the lowest temperature reached.

In consequence of the condensation of the water, heat is set free, and the temperature of the moist air rises. A stationary state is reached at a temperature t_3, when just so much water has separated that the vapour remaining is in equilibrium in contact with the drops. The subsequent changes will be slow, being due to the inflow of heat and vapour from the walls. They appear to have little effect upon the size of the drops, for the colour changes very little, and only gradually fades away; evidently through the drops becoming unequal in size. This is not difficult to understand, for the air which comes in contact with the walls of the tube, since these are covered with water, must remain saturated in spite of its rise in temperature.

If we consider 1 cub. centim. of the moist gas, we have the following equation connecting the temperature t reached at any moment with the quantity of water q which has condensed,

$$\mathrm{L}q = \mathrm{CM}\,(t - t_2),$$

where M is the mass of unit volume of the gas and C its specific heat at constant volume. It will not introduce any serious error, for the present purpose, if we neglect the heat spent in raising the temperature of the small quantity of vapour present. L is the latent heat of vaporisation, which changes slightly as the temperature changes during the process, but may be considered with sufficient exactness as equal to 606, its value at 0° C.

Now,

$$q = \rho_1 - \rho,$$

where ρ_1 is the density of the vapour just before condensation begins, and ρ the mean density of the vapour remaining uncondensed at any moment.

Thus,

$$\mathrm{L}\,(\rho_1 - \rho) = \mathrm{CM}\,(t - t_2),$$

or

$$\rho = \rho_1 - \frac{\mathrm{CM}}{\mathrm{L}}\,(t - t_2).$$

If we consider the experimental results obtained with air on March 3rd, we have, when the violet colour results, $v_2/v_1 = 1{\cdot}420$, the initial temperature being 19° C., and the pressure, when the volume $= v_2$ and the temperature $= 19°$ C., being equal to 1039 millims. of mercury. The density of air at standard temperature and pressure is ·00129 grm. per cubic centimetre.

Therefore,

$$M = {\cdot}00129 \times \frac{1039}{760} \times \frac{273}{292} = {\cdot}00165.$$

The lowest temperature calculated from the expansion is

$$t_2 = -\ 20{\cdot}2.$$

Also,

$$\rho_1 = \rho_0 \times \frac{v_1}{v_2},$$

where ρ_0 = density of saturated steam at the temperature t_1.

When $t_1 = 19°$ C.

$$\rho_0 = {\cdot}0000162,$$

therefore,

$$\rho_1 = {\cdot}0000162 \times \frac{1}{1{\cdot}42} = {\cdot}000114.$$

Now C, the specific heat of air at constant volume = ·167.

We, therefore, find for the density of the vapour, when the temperature has risen from t_2 to t,

$$\rho = {\cdot}000014 - \frac{{\cdot}167 \times {\cdot}00165\ (t - t_2)}{606}$$
$$= {\cdot}000014 - 4{\cdot}55 \times 10^{-7}\ (t - t_2).$$

If we put $t = -\ 4°$ C., we obtain for ρ the value $4{\cdot}0 \times 10^{-6}$. Now, the density of the saturated vapour at that temperature is $3{\cdot}7 \times 10^{-6}$. More vapour would, therefore, condense, and the temperature would rise further.

If $t = -\ 3°$ C., ρ calculated from the above equation $= 3{\cdot}6 \times 10^{-7}$; but the density of saturated vapour at $-\ 3°$ C. is $4{\cdot}0 \times 10^{-7}$. Condensation will, therefore, not go so far as this, but only till the temperature rises to about $-\ 3{\cdot}5°$ C., and the density of the vapour has fallen to about $3{\cdot}8 \times 10^{-6}$ grm. per cubic centimetre.

This gives us for the quantity of water which separates out from each cubic centimetre

$$\rho_1 - \rho_2 = 11{\cdot}4 \times 10^{-6} - 3{\cdot}8 \times 10^{-6}$$
$$= 7{\cdot}6 \times 10^{-6} \text{ grm.}$$

In considering how far the condensation would go, the density of vapour in equilibrium when in contact with drops of the size of those actually present should have been used, not that over a flat surface. But for drops of 5×10^{-5} centim. in radius the difference, as calculated by Lord KELVIN's formula, does not amount to more than 1 or 2 per cent., and is negligible for the present purpose.

The exact theory of the colour phenomena which are produced by clouds of small water drops such as are formed in these expansion experiments, has not, as far as I am aware, been worked out. This is especially true of the colours filling the centre of the field within the diffraction rings. Since the whole of the colour phenomena from the first appearance of small diffraction rings to the disappearance of all colour, except the bluish or greenish-white, are confined within quite a narrow range of expansions, the size of the drops evidently diminishes with great rapidity with increasing expansion.

When all diffraction colours disappear, and the fog appears white from all points of view, as it does when v_2/v_1 amounts to about 1·44, we cannot be far wrong in assuming that the diameter of the drops does not exceed one wave-length in the brightest part of the spectrum, that is, about 5×10^{-5} centim. That the absence of colour is not due to the inequality of the drops is evident from the fact that the colours are at their brightest when v_2/v_1 is only slightly less than 1·44, and from the perfect regularity of the colour changes up to this point.

Taking the diameter of the drops as 5×10^{-5} cub. centim., we obtain for the volume of each drop about 6×10^{-14} cub. centim., or its mass is 6×10^{-14} grm.

Now, we have seen that when the expansion is such as produces the sensitive tint (when $v_2/v_1 = 1{\cdot}42$), the quantity of water which separates out is about $7{\cdot}6 \times 10^{-6}$ grm. in each cubic centimetre. With greater expansions rather more must separate out. We, therefore, obtain as an inferior limit to the number of drops, when $v_2/v_1 = 1{\cdot}44$,

$$\frac{7{\cdot}6 \times 10^{-6}}{6 \times 10^{-14}} = 10^8$$

per cubic centimetre.

Effect of the Röntgen Rays on Condensation.

A statement of the results obtained when moist air is subjected to the action of the Röntgen rays, and then allowed to expand, has already been published,[*] but the experimental details were not given. The experiments were made with the second form of apparatus (fig. 2). A bulb which was giving out the X-rays energetically, as tested by a fluorescent screen, was fixed about 10 centims. from A. It was found that if expansion was made when the bulb was in action, or within a second or two after switching off the current from the induction coil, the number of drops produced was greatly increased if the expansion was such as would have caused rain-like condensation in the absence of the rays. Instead of a shower settling in one or two seconds, a fog lasting for more than a minute was produced. If, however, v_2/v_1 was below 1·25, no condensation resulted, whether the rays were acting or not.

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[*] 'Proc. Roy. Soc.,' vol. 59, p. 338, 1896.

The same results were obtained when the expansion vessel was completely wrapped up in tinfoil, which was only removed after the expansion had been made and the current had been switched off. Direct electrical action was thus excluded.

The air inside A is probably sufficiently well shielded from electrical effects by the film of water which covers the inner surface of the walls. For it was afterwards found that no effect was produced on the condensation when A was placed directly between the terminals of an induction coil while the expansion was made.

The nuclei introduced by the X-rays only persist a few seconds. No effect is noticed if the expansion be made half a minute after the current has been turned off.

It will be noticed that in these experiments the rays had to pass through the glass walls of the tube, and must, therefore, have been very much reduced in intensity.

RICHARZ* has recently shown that the condensation of the steam-jet becomes dense under the action of the X-rays. The intensity of the radiation was probably much greater in his experiments, for the rays had merely to pass through aluminium.

Hydrogen.—The action of the X-rays when hydrogen was substituted for air was afterwards investigated. It was considered unnecessary in this case, for the reasons already mentioned, to take any precautions for shielding off direct electrical action. The arrangements were in other respects exactly as in the experiments with air. The hydrogen was obtained as already described.

In the first experiments the following results were obtained :—

v_2/v_1.		Result.
1·308	No X-rays	No condensation
1·296	X-rays	Fog

Several experiments were then made with the tube exposed to the rays, each expansion being made less than the preceding one. The number of cloud-particles was observed to diminish with diminishing expansion, till, when v_2/v_1 was made equal to 1·260, only a few drops were formed, and none were seen when v_2/v_1 was equal to 1·255.

Further measurements were now made of the smallest expansion required to cause condensation when the moist hydrogen was under the influence of the X-rays.

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* 'Wied. Ann.,' vol. 59, p. 592, 1896.

v_2/v_1.		Result.
1·326	No X-rays	No condensation
1·253	X-rays	Drops very few
1·309	X-rays	Fog
1·246	X-rays	No condensation
1·259	X-rays	Shower

With the X-rays on, condensation begins when v_2/v_1 lies between 1·246 and 1·253, the density of the condensation increasing rapidly with increasing expansion.

Fresh hydrogen was now prepared. The bulb was 30 centims. from the cloud chamber.

X-RAYS on in all Cases.

v_2/v_1.	Result.
1·251	No condensation
1·254	Very few drops
1·253	Very few drops
1·251	No condensation
1·258	Drops few
1·272	Dense shower
1·282	Fog

Thus it appears that condensation begins in hydrogen originally saturated when v_2/v_1 is between 1·251 and 1·253, if the gas be exposed to the action of the X-rays. Condensation therefore begins when the supersaturation reaches the same limit as is necessary for rain-like condensation in air, the supersaturation required to produce condensation under ordinary conditions being nearly twice as great.

As in the case of air the nuclei introduced by the RÖNTGEN rays only last a few seconds. Thus immediately after obtaining condensation when v_2/v_1 was as low as 1·253, if the expansion was made while the gas was exposed to the X-rays, an experiment was made in which the current was switched off half a minute before the expansion. Although v_2/v_1 was as great as 1·315, no condensation resulted. When, however, a similar expansion was made with only a few seconds' interval a slight fog resulted.

Since the X-rays make condensation begin in hydrogen, with a much smaller expansion than is necessary in their absence, it is much more easy to detect the effect of very weak radiation than in air, where only an increase in the number of the drops results from the action of the rays.

It was found that the effect of the rays was quite noticeable, even when the bulb producing them was at a considerable distance away. For example, quite a distinct shower was produced with the bulb 120 centims. off, when v_2/v_1 was equal to 1·326, while an expansion of the same amount made immediately afterwards with the current switched off from the coil caused no condensation.

When the bulb was as far away as this it was found necessary to make rather greater expansion to bring about condensation, than when stronger radiation fell on the expansion apparatus. With the bulb 120 centims. off condensation was first detected when v_2/v_1 was equal to 1·278, none being visible with smaller expansions.

Since every nucleus, capable of promoting condensation, in vapour supersaturated to the extent reached at the completion of the expansion, becomes visible by the growth of a drop around it, it is not surprising that even weak radiation should have a visible effect.

I have not yet made any experiments* to see if X-radiation, which has not been weakened by passing through glass, makes the condensation begin at a lower supersaturation or not. The experiments of RICHARZ, to which reference has already been made, do not give us any information on this point, as the extent of the supersaturation reached in a steam-jet is unknown.

Interpretation of the Results.

The view here taken as to the meaning of the phenomena described in this paper is briefly as follows :—

In aqueous vapour in the presence of air, oxygen, nitrogen, or carbonic acid, there always exists at any moment a small number of nuclei, capable of acting as centres of condensation when the density of the vapour reaches a certain value amounting at − 6° C. to about 4·2 times that of the vapour in equilibrium over a flat surface of water at the same temperature.

The nuclei capable of acting as centres of condensation when the supersaturation lies between this lower limit and another amounting at 16° to 7·9 are comparatively few, and their number depends on the nature of the gas, for they appear to be absent in moist hydrogen. No attempts have yet been made to count the drops produced when the supersaturation lies between these limits, but from the appearance of the resulting shower they almost certainly do not amount to nearly 100 in a cubic centimetre.

When the X-rays, or such components of the radiation as are able to pass through glass, act upon moist air or hydrogen, similar nuclei are produced in much greater numbers, those of them which are the most effective in helping condensation again requiring exactly the same minimum supersaturation in order that condensation may take place upon them.

The number of nuclei capable of acting as centres of condensation when the supersaturation, even slightly, exceeds the upper limit mentioned, is, whatever gas be present, very large, and the number which come into play increases with enormous rapidity as the supersaturation is increased, reaching in air, oxygen, or nitrogen probably many millions per cubic centimetre under a tenfold supersaturation. In the other gases the observations in the colour phenomena necessary for this estimate were not made. There is no indication in these experiments of any limit to the number of drops which could be formed by sufficiently increasing the supersaturation.

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* See note at the end of the paper.

It is possible to make an approximate calculation of the size of the smallest drops which would be able to grow in vapour supersaturated to any given extent.

The formula given by Lord KELVIN* for the effect of curvature of a surface upon the pressure of the saturated vapour in contact with it only applies, in its original form, to cases where the curvature is not sufficiently great to make the density of the vapour over the curved surface differ more than very slightly from that over a flat surface. Here we wish to calculate the curvature necessary to make the equilibrium density of the vapour from four to eight times that over a flat surface.

If we assume that the supersaturated vapour obeys BOYLE'S law, and that the surface tension retains its ordinary value in the case of the very small drops with which we are dealing, there is no difficulty in seeing how the formula must be modified to allow of its being extended to such cases as the present. Both of these conditions are, unfortunately, likely to be far from being satisfied.

If we make these assumptions, the formula becomes, when the density of the vapour is as in the present case small compared with that of the liquid, identical with that obtained in a different way by R. v. HELMHOLTZ,†

$$\log_e \frac{p}{\mathrm{P}} = \frac{2\mathrm{T}}{\mathrm{R}s\theta r},$$

where p is the vapour pressure in contact with drops of radius r, P that over a flat surface at the same temperature θ; T is the surface-tension, s the density of the liquid, and R the constant in the equation $p/\rho = \mathrm{R}\theta$. Since BOYLE'S law is assumed to hold, p/P is equal to the ratio of the corresponding densities, that is, to what is here called the supersaturation S. We thus obtain for the radius of the drops just in equilibrium

$$r = \frac{2\mathrm{T}}{\mathrm{R}\theta \log_e \mathrm{S}},$$

since s in the case of water is equal to unity. R for water vapour is equal to $4{\cdot}6 \times 10^6$.

The results of the application of this formula are here given.

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[*] 'Proc. Roy. Soc.,' Edin., VII., p. 63 (1870).

[†] 'Wied. Ann.,' xxvii., p. 508 (1886).

RADIUS, in centims., of drops just large enough to grow in vapour supersaturated to the extent required to make rain-like condensation begin in the presence of Air.

$t°$ C.	θ.	T.	S.	r.
-10	263	77	4·35	$8{\cdot}7\times10^{-8}$
-6	267	76	4·2	$8{\cdot}6\times10^{-8}$
$+2$	275	75	4·0	$8{\cdot}6\times10^{-8}$

r thus appears to be constant over the range of temperature $-10°$ C. to $+2°$ C. The value obtained for r is not changed by as much as 3 per cent. when the air is replaced by nitrogen, oxygen, or CO_2, or by hydrogen under the action of the X-rays.

RADIUS, in centims., of drops just large enough to grow when supersaturation is sufficient to make the dense condensation begin in Air, Oxygen, Nitrogen, or Hydrogen.

$t°$ C.	θ.	T.	S.	r.
-16	257	78	7·9	$6{\cdot}4\times10^{-8}$

If we consider the difference in the value found for S in CO_2 to be real, and not due merely to the error in the calculation of the cooling, due to deviation of CO_2 from the condition of a perfect gas, we find that r in CO_2 is about 3 per cent. greater than in these other gases.

RADIUS, in centims., of drops just large enough to grow when the supersaturation is such that the sensitive tint is produced in the presence of Air or Oxygen.

$t°$ C.	θ.	T.	S.	r.
-19	254	79	9·9	$5{\cdot}9\times10^{-8}$

The difference when nitrogen is substituted for Air or Oxygen is exceedingly small.

It cannot be assumed that the surface tension retains its ordinary value in drops of such small radii, which are not great compared with molecular dimensions. We know, in fact, from the behaviour of thin films, that it does not. These numbers therefore can only be considered as giving a very rough approximation to the absolute size of the water drops which would actually be in equilibrium in vapour of the various degrees of supersaturation.

They furnish, however, a convenient means of expressing the relative efficiency of the nuclei in helping condensation. Thus, the nuclei producing rain-like condensation are equivalent in their effect on the condensation, to water drops of radii between $6{\cdot}4 \times 10^{-8}$ and $8{\cdot}7 \times 10^{-8}$ centim. There are, as we have seen, certainly not more than 100 of these in each cubic centimetre of moist air, and they are absent in hydrogen. The nuclei equivalent to water drops whose radii lie between the narrow limits $5{\cdot}9 \times 10^{-8}$ and $6{\cdot}4 \times 10^{-8}$ centim. amount to many millions per cubic centimetre.

It is difficult to account for the immense number of these latter nuclei, otherwise than on the view that they actually are simply small aggregates of water molecules, such as may come into existence momentarily through encounters of the molecules. On this view the dimensions of the molecules cannot be small compared with 6×10^{-8} centim. BARUS* states that if it were possible to measure the supersaturation required to make steam condense in the absence of dust, the dimensions of the molecules could be calculated with the aid of LORD KELVIN'S formula. Probably he takes some such view as that here suggested.

The nuclei which bring about the rain-like condensation, and the greater number of which appear to be equivalent in their power of causing condensation to water drops of not much less than $8{\cdot}7 \times 10^{-8}$ centim. are probably of a different character.

As, however, I am continuing these experiments, it would be premature at the present stage to discuss the various views that might be held as to their nature.

[*Note added July* 22, 1897.

Further Experiments on the Action of the X-rays.—I have lately repeated the experiments on air, using an expansion apparatus provided with a window of very thin aluminium, so arranged that the whole of the contents of the tube were exposed to the rays of a suitably placed Röntgen lamp.

This gave results identical with those already obtained, no condensation resulting when the air was expanded while exposed to the rays unless v_2/v_1 exceeded 1·25, while with expansions even slightly exceeding this, a comparatively dense fog resulted; only a few scattered drops appearing with similar expansions in the absence of the rays.

As was to be expected, much denser fogs were obtained under the action of the rays with this apparatus than with that formerly used.

A glass plate of 7 millims. thick, placed over the window, appeared to cut off the effect of the rays completely.]

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* 'Phil. Mag.,' vol. 38, p. 34 (1894); also "Report on the Condensation of Atmospheric Moisture." U. S. Department of Agriculture, Weather Bureau, 1895.

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—— Part II...	3	0	0
1876. Part I...	2	8	0
—— Part II...	2	8	0
1877. Part I...	1	16	0
—— Part II...	2	5	0
Vol. 168 (extra)	3	0	0
1878. Part I...	1	16	0
1878. Part II...	3	0	0
1879. Part I...	2	0	0
—— Part II...	1	12	0
1880. Part I...	2	5	0
—— Part II...	2	0	0
—— Part III...	1	1	0
1881. Part I...	2	10	0
—— Part II...	1	10	0
—— Part III...	2	2	0
1882. Part I...	1	14	0
—— Part II...	2	0	0
—— Part III...	2	10	0
—— Part IV...	1	0	0
1883. Part I...	1	10	0
—— Part II...	2	10	0
—— Part III...	1	12	0
1884. Part I...	1	8	0
—— Part II...	1	16	0
1885. Part I...	2	10	0
—— Part II...	2	5	0
1886. Part I...	1	8	0
—— Part II...	1	15	0
1887. (A.)	1	3	0
—— (B.)	1	16	0
1888. (A.)	1	10	0
—— (B.)	2	17	6
1889. (A.)	1	18	0
—— (B.)	1	14	0
1890. (A.)	1	16	6
—— (B.)	1	5	0
1891. (A.)	2	2	0
—— (B.)	3	3	0
1892. (A.)	2	1	0
—— (B.)	2	2	0
1893. (A.)	3	14	0
—— (B.)	2	13	0
1894. (A.) Pt. I.	1	5	0
—— (A.) Pt. II.	1	10	0
—— (B.) Pt. I.	3	10	0
—— (B.) Pt. II.	1	11	6
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—— (A.) Pt. II.	1	3	6
—— (B.) Pt. I.	1	15	0
—— (B.) Pt. II.	0	16	6
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—— (A) Vol. 188.	1	9	0
—— (B) Vol. 187.	0	19	0
1897 (A) Vol. 189.	1	0	0
—— (B) Vol. 188.	0	19	6

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